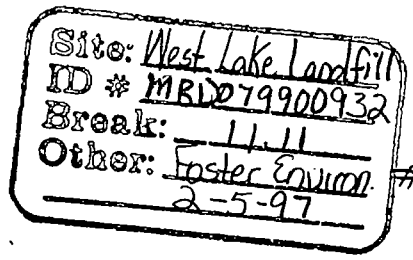
FOSTER

Environmental Services



#042

0714
SF

February 5, 1997

Mr. Steven Kinser, Remedial Project Manager
U.S. Environmental Protection Agency
Superfund Branch
Region VII
726 Minnesota Avenue
Kansas City, KS 66101

RE: SOPS FOR THE WEST LAKE LANDFILL OPERABLE UNIT 2, BRIDGETON, MO

Dear Mr. Kinser:

Enclosed are three copies of a Quality Assurance Plan and Standard Operating Procedures (SOPs) for TriMatrix Laboratories. The documents are submitted by Foster Environmental Services on behalf of Laidlaw Waste Systems, Inc.

Also included are three copies of Pace Analytical's SOPs for hardness and sulfide analysis. These SOPs were inadvertently omitted from the previous SOP package.

Should you have any questions please feel free to call me at (609) 492-6747.

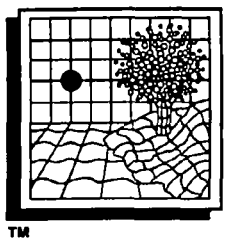
Sincerely,

Diane Foster

cc: Doug Borro, Laidlaw Waste Systems, Inc.
Ward Herst, Golder Associates Inc.

P.O. Box 1245 • Beach Haven, New Jersey 08008 • (609)492-6747

OFFICIAL COPY RED STAMP INDICATES ORIGINAL



SOUTHWEST LABORATORY OF OKLAHOMA, INC.

STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF TOTAL ALPHA EMITTING RADIUM

RD102

REV1.1 — 1/01/97

Document Control #SWL-RD102- 004

CONTROLLED DOCUMENT: DO *NOT* COPY!

APPROVALS BY:

Name: Kert Surface *Title: Radiochemistry Mgr.*

Signature: _____ *Date:* 1/2/97

Name: Chuck Hoover *Title: QA/QC Officer*

Signature: _____ *Date:* 1/2/97

Table of Contents

I PURPOSE

A. The purpose of this instruction is to provide a method for analysis of total alpha-emitting radioisotopes of radium, namely radium-223, radium-224, and radium-226 in waters.

II APPLICABILITY

A. This instruction applies to the determination of total alpha-emitting radium in water. This method also applies to the determination of Ra-226 as this isotope is a common alpha emitter.

III RESPONSIBILITIES

A. The radiochemistry analyst who is experienced in standard wet preparation methods and who is trained in the use of this procedure shall be permitted to perform this procedure.

IV EQUIPMENT REQUIRED

A. Low background alpha beta proportional counter.

B. Analytical Balance.

C. Centrifuge.

D. Hot water bath.

V REAGENTS AND CHEMICALS REQUIRED

A. Barium carrier, 16 mg/ml: Dissolve 28.46g $BaCl_2.2H_2O$ in water, add 5 ml 16 N HNO_3, and dilute to 1 liter with water in a volumetric flask. (Standardize)

B. Lead carrier, 1.5 mg/ml: Dilute 10.0 ml $Pb(NO_3)_2$ (15 mg/ml) to 100 ml with water in a volumetric flask. OR: Dissolve 2.397g $Pb(NO_3)_2$ in water, add 0.5 ml 16 N HNO_3, and dilute to 1 liter.

C. Acetic acid, 17.4N : CH_3COOH (glacial), sp. gr. 1.06, 99.5%.

D. Ammonium hydroxide, 15N: NH_4OH (conc.), sp. gr. 0.9, 50%.

E. Ammonium hydroxide, 5N: Mix 1 volume 15N NH_4OH with 2 volumes water.

F. Nitric acid, 16N: HNO_3 (conc.) sp. gr. 1.42, 70%

G. Sulfuric acid, 36N

H. Disodium EDTA, 0.25 M: Dissolve 40g NaOH in about 750 ml water, and slowly add 186g $Na_2C_{10}H_{14}O_8N_2O.2H_2O$ while stirring. After the salt is in solution, filter through a coarse filter paper and dilute to 2 liters with water in a volumetric flask.

VI PRECAUTIONS

A. Standard safety and radiological precautions should be observed.

VII INSTRUCTIONS

A. Take 1 liter of sample. (If sample is less than 1 liter, dilute up to 1 liter. Also, if sample is turbid or contains solvents, filter through a filter pad.) Add Ra-226 standard to the standard. Prepare a blank sample using DI water.

B. Add the following:

10 ml conc. H_2SO_4

25 ml conc. HCl

5 ml Na/K sulfate solution

1-5 mls $HClO_4$, if organics are present and depending upon the amount of organics present.

C. Add: 1 ml Pb carrier (1.5 mg/ml) (sero. pipette) 3 mls Y carrier (10 mg/ml) (sero. pipette).

D. Boil solution about 30 min.

E. To the boiling solution 2 mls $BaCl_2$ (16 mg/ml) in 2 portions spaced about 10 min apart. (Use a volumetric pipette.)

F. Return to a boil and let boil about 30 more minutes.

G. While solution is still warm, filter into a 47 mm GA-6(.45 um) filter using 0.5% H_2SO_4 as a wash/rinse solution.

H. Carefully place the filter with the precipitate into a 50 ml centrifuge tube. Add: 15 ml 16N HNO_3. Heat gently in hot water until the filter dissolves. Centrifuge and discard the supernatant.

I. Wash precipitate twice with 15 ml 16 N HNO_3, discarding washes. Wash precipitate twice with 15 mls D.I. water, discarding washes.

J. Add 20 ml 0.25 M Na_2EDTA.

K. Heat in hot water bath to clear.

L. Add 2 ml 17.4 N CH_3COOH (glacial acetic acid) slowly, then add 2 ml excess. RECORD TIME of the $BaSO_4$ precipitation, as this is the beginning of the radium decay.

M. Digest 5 - 10 minutes in the hot water bath, cool, centrifuge, and discard the supernate.

N. Wash precipitate 3 times with 15ml water, discarding washes.

O. Take precipitate up in 5 ml H_2O and transfer to tared stainless steel planchets. Record tare and gross weights in data pages.

P. Dry under infrared light, cool, weigh, and alpha count. Record the time at midpoint of count, as this is the end of the decay.

Q. Submit for Alpha counting. Fill data pages and submit for calculations.

R. Calculate the total alpha-emitting radium activity, A, in picocuries per volume used in "V" below as follows or calculate the radium-226 activity, A (which would include any radium-224 and radium-223 that is present), in picocuries per volume used in "V" below as follows:

$$A = \frac{B - C}{(2.22)(E)(V)(R)(I)}$$

where:

B=gross alpha count per minute

C=count per minute of background gross alpha

R=chemical yield = $BaSO_4$ observed / $BaSO_4$ expected

I=ingrowth factor for Radon

E=detecter efficiency

V=sample volume

2.22=conversion factor from dpm to pCi

VIII RECORDS

A. Retain all raw data and any supporting printouts and or calculations in job folders.

IX ATTACHMENTS

A. Attachment 1 - References

B. Attachment 2 - Total Radium Prep

C. Attachment 3 - Calculation Form

Attachment 1

REFERENCES

1. Standard Methods for the Examination of Water & Wastewater, 12th edition, 1965, pp 349-352.

2. A.S. Goldin, Determination of Dissolved Radium, Analytical Chemistry, Vol 33, 1961, pp 406.

3. Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, August, 1980.EPA 903.0

4. SW-846, Third Edition, September 1986, Method 9315.

Attachment 2

TOTAL RADIUM PREP

Total Alpha Radium Prep, SWL-RD102

TOTAL RADIUM PREP FORM (102-ATT2.DOC) Book # RD102-PRP-_1_

Prep Date:_____ Analyst: ___ Batch ID: _____ Verified ___

Sample Number	Volume	Tare Weight	Gross Weight	Net Weight	Notes

Expected BaSO4 or Ba-133._____

Standard ID/ Activity:_____

Amount Used :_____

Ba Carrier/tracer ID :_____

COMMENTS:_____

Attachment 3

CALCULATION FORM

Total Alpha Radium Calc., SWL-RD102

TOTAL RADIUM CALC. FORM (102-ATT3.DOC)

Prep Date:_____ Analyst: ___ Batch ID: _____ Verified ___

Sample Number	Counts	Count Time	Inst. Eff.	Vol.	BKG Counts	BKG Time	ACTIVITY, ERROR EST.	LLD

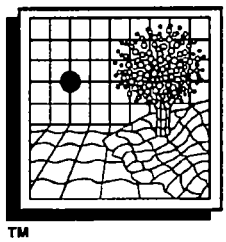
Expected BaSO4 :_____ Results STD:_____

Standard ID/ Activity:_____ BLK:_____

Amount Used :_____ DUP 1:_____

Ba Carrier/tracer ID :_____ DUP 2:_____

COMMENTS:_____



SOUTHWEST LABORATORY OF OKLAHOMA, INC.

STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF ISOTOPIC THORIUM

RD107

REV 1.0 — 7/17/96

Document Control #SWL-RD107-004

CONTROLLED DOCUMENT: DO NOT COPY!

APPROVALS BY:

Name: Kert Surface *Title: Radiochemistry Mgr.*

Signature: Kert Surface

Name: Chuck Hoover *Title: QA/QC Officer*

Signature: Chuck Hoover

Table of Contents

I. PURPOSE

A. This procedure gives instructions for the analysis of Isotopic Thorium by alpha spectroscopy.

II. APPLICABILITY

A. This procedure provides separation of the element from other interfering analytes by ion-exchange techniques.

III. RESPONSIBILITIES

A. The radiochemistry analyst who is experienced in standard wet preparation methods and who is trained in the use of this procedure shall be permitted to perform this procedure.

IV. EQUIPMENT REQUIRED

A. Alpha Spectrometer.

V. REAGENTS AND CHEMICALS REQUIRED

A. Reagents: All solutions are to be stored in polypropylene bottles.

1. Ferric chloride solution:

   27 gm Ferric Chloride

   10 ml 12N Hydrochloric Acid

   Make to 1 Liter with Deionized Water

2. Cerium Carrier:

   1.5494g $Ce(NO_3)_3$

   Make to 1 liter with Deionized Water.

3. 80 % Ethanol:

   800 mls 95 % Ethanol

   Make to 1 liter with Deionized Water

4. 5 % Ascorbic Acid:

   5 g Ascorbic Acid

   Make to 100 mls with Deionized Water

5. Substrate Suspension

   1 ml of (10mg of Nd/ml) solution

   20 ml of 12N Hydrochloric Acid

   Make to 400ml with Deionized Water

   then add 10ml of 29N Hydrofluoric Acid

   1 to 2 ml of Carbon Suspension (with swirling)

   Make to 500ml with Deionized Water

   Note:Suspension should be placed in a sonic bath for 15 minutes each day before use.

6. Carbon suspension:

   One 47 mm GA-6 dissolve in 5 mls Concentrated H_2SO_4.

   Dilute to 50 mls with Dionized Water.

VI. PRECAUTIONS

A. Standard safety and radiological precautions should be observed.

VII. INSTRUCTIONS

A. Procedure

1. Place an aliquot of sample in a 1 L beaker.

2. Add ~25ml of 12N Hydrochloric Acid

   5 ml of Iron carrier (Ferric Chloride Solution.)

   ~5ml Hydrogen Peroxide (30%)

Standards and Tracers (Use Th-234 tracer from SWL-RD111 "Thorium-234 Preparation".) Do not add tracers to soil samples that have been digested under SWL-RD126 for alpha spectroscopy analysis. Tracers should have been added prior to digestion. Assure that tracers were added to these samples prior to digestion before continuing with the next step. If tracers were not added prior to digestion, report the deficiency to the laboratory supervisor and arrange to have the sample digestion repeated.

3. Make up solution to 800ml and cover with watchglass.

4. Heat to boiling on a hot plate for 45 minutes to one hour, stirring frequently to evolve all Carbon Dioxide.

5. Slowly and with stirring add 15N (conc.) Ammonium Hydroxide until the red Iron Hydroxide precipitate drops out of solution.

6. Return to hotplate and cook for another 15 to 20 minutes.

7. Remove from the hotplate and allow to cool.

8. Pour off as much of the liquid as possible and centrifuge, discarding the supernate.

9. Dissolve the precipitate in 12N Hydrochloric Acid.

10. Prepare 1 x 2 anion exchange column by pouring one 50 ml portion of 9N HCl and discarding effluent.

11. Pour the prepared sample from Step # 9 into the column. Stir the sample down into the resin with a glass stir rod rinsing the rod into the column with 9N HCl, saving the effluent in a clean, labeled 250 ml beaker.

12. Pour two separate 50 ml portions of 9N HCl through column, saving them into same beaker from Step # 11.

13. Evaporate sample in beaker to dry.

14. Add: 50 mls of 7.2 N HNO_3 + 5 drops H_2O_2 cover the beaker and reflux for 45 minutes (low heat).

15. Add: 3 drops of H_2O_2 (30 %) and reflux for 15 minutes more.

16. Pour two separate 50 ml portions of 1.2 N HCl through column, discarding effluents.

17. Pour two separate 50 ml portions of 7.2 N HNO_3 through column discarding effluents.

18. Pour sample into column, discarding effluent.

19. Pour two separate 50 ml portions of 7.2 N HNO_3 through column discarding effluents.

20. Pour two separate 50 ml portions of 9N HCl through column, saving effluents in 250 ml beaker.

21. Evaporate sample to dry.

22. Add 10 of 20 mg/ml $NaHSO_4$ to sample and evaporate to dry.

23. Dissolve sample in 10 mls of 3 M HCl.

24. Heat sample to just boiling, and transfer to a 40 ml centrifuge tube with a minimum water rinse.

25. Add 2 drops of 5% ascorbic acid.

26. Add 0.1 ml of Ce-Carrier (50 ug) and 2 ml of concentrated HF. Let stand for a minimum of 30 minutes.

27. Filter onto HT-200 filter using the following:

    80% Ethanol (4-5ml)

    10ml Resl Substrate (stir well)

    sample (swirl first)

    H_2O Rinse (1-2 mls)

    80% Ethanol (4-5ml)

    Let sample dry.

28. Submit for Alpha Spectroscopy, and fill out calculation pages and submit for calculations.

29. Calculate each isotope of thorium activity, A, in picocuries per voume used in "V" below as follows:

$$A = \frac{\frac{SC}{T} - \frac{BC}{T}}{\frac{IC/T}{Idpm} \times V \times 2.22}$$

Where:

SC=sample counts

BC=background counts

T=time in minutes

V=sample volume

IC=internal tracer counts

Idpm=internal tracer dpm

2.22=conversion factor from dpm to pCi.

VII. RECORDS

A. Retain all raw data and any supporting printouts and or calculation in job folders.

IX. ATTACHMENTS

A. Attachment 1 - References

B. Attachment 2 - Isotopic Thorium Prep

C. Attachment 3 - Thorium Calculation Form

Attachment 1

REFERENCES

1.EMSL-LV-0539-17

2.SWL-RD111 "Thorium 234 Preparation"

Attachment 2

ISOTOPIC THORIUM

Prep Date:_____ Analyst: ___ Batch ID: _____ Verified ___

Sample Number	Volume	Sample Matrix	Column Number	Notes

Standard ID/ Activity :_____ Results STD:_____

Amount used :_____ BLK:_____

Thorium Tracer ID/ Activity :_____ DUP 1:_____

Amount Used :_____ DUP 2:_

Attachment 3

THORIUM CALCULATION FORM

Prep Date:___________ Analyst: ___ Batch ID: ___________ Verified ___

Spl ID	Isotope	Sample Gross Cnts	Tracer Counts	Samp Time (min)	Vol ml , g	Bkg Cnts	Bkg Time	Tracer DPM	Activity Error Estimate	M D A
	Th-228								+-	
	Th-230								+-	
	Th-232								+-	
	Th-228								+-	
	Th-230								+-	
	Th-232								+-	
	Th-228								+-	
	Th-230								+-	
	Th-232								+-	
	Th-228								+-	
	Th-230								+-	
	Th-232								+-	
	Th-228								+-	
	Th-230								+-	
	Th-232								+-	
	Th-228								+-	
	Th-230								+-	
	Th-232								+-	
	Th-228								+-	
	Th-230								+-	
	Th-232								+-	

Standard ID :______________________________ Std Activity : Th-228:______________

Amount used :______________________________ Th-230 :______________

Thorium Tracer ID/ Activity :______________________________ Th-232:______________

SOUTHWEST LABORATORY OF OKLAHOMA, INC.

STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF ISOTOPIC URANIUM

RD108

REV 1.0 — 07/17/96

Document Control #SWL-RD108-004

CONTROLLED DOCUMENT: DO NOT COPY!

APPROVALS BY:

Name: Kert Surface *Title: Radiochemistry Manager*

Signature: Kert Surface

Name: Chuck Hoover *Title: QA/QC Officer*

Signature: Chuck Hoover

Table of Contents

I. PURPOSE

A. This procedure gives instructions for the analysis of isotopic uranium by alpha spectroscopy.

II. APPLICABILITY

A. This procedure provides separation of the element from other interfering analytes by ion-exchange techniques.

III. RESPONSIBILITIES

A. The radiochemistry analyst who is experienced in standard wet preparation methods and who is trained in the use of this procedure shall be permitted to perform this procedure.

IV. EQUIPMENT REQUIRED

A. Alpha Spectrometer

V. REAGENTS AND CHEMICALS REQUIRED

A. Reagents: All solutions are to be stored in polypropylene bottles.

1. Ferric chloride solution:

   27g Ferric Chloride

   10ml 12N Hydrochloric Acid

   Make to 1 Liter with Deionized Water

2. Neodymium Chloride (10mgNd/ml)

   25 ml 12N Hydrochlorid Acid

   1.17 g of Neodymium Oxide

   Heat on hotplate until the Neodymium Oxide is in solution

   Make 100 ml with Deionized Water.

3. Neodymium Chloride (0.5mg Nd/ml)

   5ml of (10mg of Nd/ml) solution

   Make to 100 ml with Deionized Water.

4. Substrate Suspension

1ml of (10mg of Nd/ml) solution

20 ml of 12N Hydrochloric Acid

Make to 400ml with Deionized Water

then add 10 ml of 29N Hydrofluoric Acid.

1 to 2 ml of Carbon suspension (with swirling)

Make to 500ml with Deionized Water.

Note: Suspension should be placed in a sonic bath for 15 minutes each day before use.

5. 4% Hydrofluoric Acid

   40ml 29N Hydrofluoric Acid

   Make to 500ml with Deionized Water.

6. 80% Ethanol:

   800 mls 95% Ethanol

   Make to 1 liter with Deionized Water.

VI. PRECAUTIONS

A. Standard safety and radiological precautions should be observed.

VII. INSTRUCTIONS

A. Procedure

1. Place an aliquot of sample in a 1 L beaker.

2. Add ~25ml of 12N Hydrochloric Acid

   5 ml of Iron carrier (Ferric Chloride Solution.)

   ~5ml Hydrogen Peroxide (30%)

   Standards and Tracers (use U-232 tracer)

Do not add tracers to soil samples that have been digested under SWL-RD126 for alpha spectroscopy analysis. Tracers should have been added prior to digestion. Assure that tracers were added to these samples prior to digestion before continuing with the next step. If tracers were not added prior to digestion, report the deficiency to the laboratory supervisor and arrange to have the sample digestion repeated.

3. Make up solution to 800ml and cover with watchglass.

4. Heat to boiling on a hot plate for 45 minutes to one hour, stirring frequently to evolve all Carbon Dioxide.

5. Slowly and with stirring add 15N (conc.) Ammonium Hydroxide until the red Iron Hydroxide precipitate drops out of solution.

6. Return to hotplate and cook for another 15 to 20 minutes.

7. Remove from the hotplate and allow to cool.

8. Pour off as much of the liquid as possible and centrifuge, discarding the supernate.

9. Dissolve the precipitate in 12N Hydrochloric Acid.

10. Pour the sample into an anion exchange column.

Note on column: Column should use 1x2 resin which has been prepared with 9N Hydrochloric Acid and Hydrogen Peroxide.

Stir the sample down into the resin with a glass stir rod rinsing the rod into the column with 9N Hydrochloric Acid, discarding the effluent .

11. Wash with 3 20-30ml portions of 9N Hydrochloric Acid and discard effluent.

Note on washes: Each wash should not be carried out until top of the resin has cleared the previous wash.

12. Wash with 1 20-30 ml portion of 9N hydrochloric Acid with 2-3 drops of Hydrogen Peroxide (30%) and discard effluent.

13. Wash with 3 20-30ml portions of Hydrochloric/Hydroiodic Acid solution, stirring the first wash down into the resin with a stirring rod and rinsing the rod into the column with the HCI/HI solution and discard the effluent.

14. Wash with 1 20-30ml portions of 9N Hydrochloric Acid and discard effluent.

15. Wash with 2 20-30ml portions of 1.2N Hydrochloric Acid and save the effluent in a clean, labeled 250ml beaker.

16. Wash with 3-4 20-30ml portions of 0.1N Hydrochloric Acid until the volume of the beaker reaches ~150ml and save the effluent.

17. Heat the effluent to boiling and evaporate to dryness.

18. Wash down the sides of the beaker with 6N Hydrochloric Acid (~50ml), heat to boiling, and evaporate to dryness.

19. Wash down the sides of the beaker with 1.2N Hydrochloric Acid (~50ml.)

20. To the beaker add:

    2 drops 0.1% Safranine-O

    2 drops 20% Titanium Trichloride

21. Cover the beaker and reflux, reducing the volume to ~10ml.

22. While the sample is still hot, transfer to a centrifuge tube with 2% Hydrochloric Acid and bring volume to ~25ml with the 2% Hydrochloric Acid.

23. To the centrifuge tube add:

    1 ml 12N Hydrochloric Acid (swirl)

    1 drop 0.1% Safranine-O (swirl)

    1 drop 20% Titanium Trichloride (swirl)

    5 drops Neodynium Chloride (0.5mg/ml) (swirl)

    5ml 29N Hydrofluoric Acid (cap and swirl)

24. Let sample stand at least 30 minutes in a cold water bath.

25. Filter onto HT-200 filter using the following:

    80% Ethanol (4-5ml)

    10ml Substrate Susp. (stir well)

    sample (swirl first)

    4% HF (3-5ml)

    80% Ethanol (4-5ml)

26. Dry sample

27. Submit for Alpha Spectroscopy, and fill out calculation pages and submit for calculations.

28. Calculate each isotope of uranium activity, A, in picocuries per volume used in "V" below as follows:

$$A = \frac{\frac{SC}{T} - \frac{BC}{T}}{((IC/T)/Idpm) \times V \times 2.22}$$

Where:

SC=sample counts

BC=background counts

T=time in minutes

V=sample volume

IC=internal tracer counts

Idpm=internal tracer dpm

2.22=conversion factor from dpm to pCi.

VIII. RECORDS

A. Retain all raw data and any supporting printouts and or calculations in job folders.

IX. ATTACHMENTS

A. Attachment 1 - References

B. Attachment 2 - Isotopic Uranium Prep

C. Attachment 3 - Uranium Calculation Form

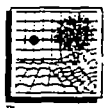
Attachment 1

REFERENCES

1.EMSL-LV-0539-17

Attachment 2

ISOTOPIC URANIUM PREP



Isotopic Uranium Prep, SWL-RD108

ISOTOPIC URANIUM PREP FORM (108-ATT2.DOC) Book # RD108-PRP-__1__

Prep Date:_____ Analyst: ___ Batch ID: _____ Verified ___

Sample Number	Volume	Sample Matrix	Column Number	Notes

Standard ID/ Activity :_____ Results STD:_____

Amount used :_____ BLK:_____

Uranium Tracer ID/ Activity :_____ DUP 1:_____

Amount Used :_____ DUP 2:_____

Attachment 3

URANIUM CALCULATION FORM

Isotopic Uranium Calc., SWL-RD108

ISOTOPIC URANIUM CALC. FORM (108-ATT3.DOC)

Prep Date:__________ Analyst: ___ Batch ID: __________ Verified ___

Spl ID	Isotope	Sample Gross Cnts.	Tracer Counts	Samp Time (min)	Vol. ml , g	Bkg Cnts	Bkg Time	Tracer DPM	Activity Error Estimate	MDA
	U-234								+-	
	U-235								+-	
	U-238								+-	
	U-234								+-	
	U-235								+-	
	U-238								+-	
	U-234								+-	
	U-235								+-	
	U-238								+-	
	U-234								+-	
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	U-234								+-	
	U-235								+-	
	U-238								+-	
	U-234								+-	
	U-235								+-	
	U-238								+-	
	U-234								+-	
	U-235								+-	
	U-238								+-	

Standard ID :______________________ Std Activity : U-234 :__________

Amount used :______________________ U-235 :__________

Uranium Tracer ID/ Activity :______________ U-238 :__________

Amount Used :______________________

STANDARD OPERATING PROCEDURE

TITLE: *GAS FLOW PROPORTIONAL COUNTER - ANALYSIS OF ALPHA AND BETA EMITTING RADIONUCLIDES*

FORM NO.:NONE

PREPARED BY:	Toby Carroll		
APPROVED BY:	TECHNICAL MANAGER		DATE 4/9/96
	HEALTH/SAFEY OFFICER		DATE 4-9-96
	QA/QC OFFICER		DATE 4/9/96

HISTORY: Rev 0, 5/10/93, Rev 3, 7\29\93; Rev 4, 3/2/94, PCN #149; *Rev 5, 4/25/95, PCN #466;*

1.0 SUMMARY, SCOPE, AND APPLICATION

1.1 SCOPE AND APPLICATION

This procedure describes the steps necessary to perform alpha and beta emissions analysis of samples of various media using the Tennelec LB 4100W gas flow proportional counting system. Samples will normally be liquids (primarily water) and solids (primarily soil or sand) evaporated onto planchetts or precipitated onto filters. This procedure is applicable to all gross alpha/beta analyses and certain specific beta analyses (such as ^{90}Sr) and alpha analyses (such as Total Radium) performed on the Tennelec LB4100W at ATI's Environmental Radiochemistry Laboratory.

1.2 SUMMARY OF METHOD

Alpha and beta particle emissions from the sample container produce ionization in a gas-filled chamber, generating a small electronic pulse for each interaction. The pulse height is dependent upon the incident energy of the particle. Since alpha and beta particles are normally emitted at widely separated energies, the instrument is able to discriminate between the alpha and beta particle interactions. The instrument provides raw counting information to a computer and spreadsheet-based analysis program, generating results in units of radioactivity per unit sample volume.

2.0 DISCUSSION/COMMENTS

ATI's Environmental Radiochemistry Laboratory is utilizing 3 PC-based low background counting systems for acquisition of alpha and beta particle emissions data from samples contained on 2 inch planchetts. These systems are each controlled by an 80486 personal computer, each having an IEEE/GPIB interface card and manufacturer-provided control and analysis software. One of these counting systems is a manually operated Tennelec model LB 4100W. The counter operations and subsequent data analysis are controlled through a series of menu-driven applications. This procedure is applicable to the LB 4100W.

3.0 APPARATUS

This procedure is conducted with the use of installed alpha/beta detection and analysis equipment consisting of a 16 detector manual counter (samples are counted simultaneously). The detectors are mounted in cavities of lead bricks for the reduction of ambient background radiation. This system is served by an 80486 personal computer, menu-based control and analysis software, and attendant printer.

STANDARD OPERATING PROCEDURE

TITLE: *GAS FLOW PROPORTIONAL COUNTER - ANALYSIS OF ALPHA AND BETA EMITTING RADIONUCLIDES*

FORM NO.:NONE

4.0 PROCEDURES

4.1 OPERATING CONDITIONS

Samples shall only be analyzed on LB 4100W detectors when the detector is in proper:

instrument calibration
analyte calibration
(See ATI SOP770FC)

and these daily checks pass:

Background check
Efficiency check
(See ATI SOP770FC)

Detectors must operate within the specifications given in ATI SOP770FC.

4.2 SAMPLE PREPARATION

Samples to be analyzed by this method will have been prepared by radiochemical procedures applicable to the radionuclide(s) being evaluated. Sample preparation may be limited to quantitative distribution into a planchett or may be as complex as a complete digestion and chemical separation. See appropriate radiochemical procedure(s).

4.3 PROCEDURE

4.3.1 The applications software for this instrument is a Windows(TM) product. It is assumed that the operator of the software is familiar with the basic operation of Windows(TM).

4.3.2 Loading Samples

Detectors must meet the conditions in 4.1

4.3.2.1 pull out drawer

4.3.2.2 place samples in holders (Avoid disturbing the sample to prevent detector contamination)

4.3.2.3 close drawer then turn knob to the locked position

4.3.2.4 note the detector position for each sample on the benchsheet and initial benchsheet

STANDARD OPERATING PROCEDURE

TITLE: *GAS FLOW PROPORTIONAL COUNTER - ANALYSIS OF ALPHA AND BETA EMITTING RADIONUCLIDES*

FORM NO.:NONE

4.3.2.5 note the filename on the benchsheet in the proper place
(Filename should be both unique and descriptive. The filename usually contains the test, current date, and the run # for that analyte on that day. For example, the second run on 05/15/95 of Sr in soil could have the filename SrS0515B.xld.)

4.3.2.6 note the count date/time on benchsheet

4.3.2.7 note appropriate information in LB4100 run logbook

4.3.3 Starting Count

4.3.3.1 click the right button of the mouse on the lb4100 icon to get the main menu

4.3.3.2 choose "CREATE BATCH"

4.3.3.3 using mouse single- click on the detectors to be used

4.3.3.4 using mouse choose the analysis to be run on the chosen detectors (Sr in soil,Total Radium, etc.)

4.3.3.5 type in the chosen filename and batch ID
(Filename and batch ID should be both unique and descriptive. The filename usually contains the test, current date, and the run # for that analyte on that day. For example, the second run on 05/15/95 of Sr in soil could have the filename SrS0515B.xld. The batch ID would simply give the workorder # and samples, for example 95-05-123,01-05.)

4.3.3.6 click on "RUN"
Sample ID Entry window will now appear.

4.3.3.7 enter appropriate sample ID for each detector

4.3.3.8 click on "DONE"
Computer will load appropriate detector information(bkg.,eff.,attn.) then the sample application data entry window will appear:

4.3.3.9 enter sample residual mass in milligrams

4.3.3.10 enter sample volume in liters or grams

4.3.3.11 click on "CLOSE"
Detectors are now acquiring data.

4.3.3.12 Check that appropriate information has been entered into LB4100 run logbook
When the counting time has expired, the program will begin beeping and the detector icons in the windows screen corresponding to the detectors whose counts are finished will blink. When all samples within the batch are finished;

4.3.3.13 using lb4100 menu choose "UNIT STATUS"

STANDARD OPERATING PROCEDURE

TITLE: *GAS FLOW PROPORTIONAL COUNTER - ANALYSIS OF ALPHA AND BETA EMITTING RADIONUCLIDES*

FORM NO.:NONE

4.3.3.14 single click on finished detectors or the batch ID description for the finished samples

4.3.3.15 click on "FREE"
Choosing "FREE" releases the detector from the chosen application.

4.3.3.16 turn knob on LB4100 to unlocked position

4.3.3.17 take samples off holders double checking detector position from the benchsheet

Avoid handling samples as much as possible so as not to cause cross contamination between samples and possible detector contamination.

4.3.3.18 store samples in appropriate place until time of disposal

4.3.4 Raw Data Output

From the LB4100 main menu as described in 4.3.3.1, choose "Data Output", then select the data file used to name the batch in step 4.3.2.3 above. The program will present the data on the screen. Click on "print". The program will generate a hardcopy of the data and an ASCII file of the same name as the spreadsheet, with a ".ASC" suffix.

Check the printout to ensure the accuracy of the following items:

4.3.4.1 sample ID and detector position match benchsheet

4.3.4.2 count time and date match benchsheet

4.3.4.3 sample mass and volume match benchsheet

4.3.4.4 blank, matrix spike, and blank spike activity within appropriate limits

4.3.4.5 duplicate's and corresponding sample's activity agree within appropriate limits

If there is any error on the printout see your supervisor immediately.

4.3.5 Database Entry

4.3.5.1 In the Windows main menu choose the data reporting option appropriate to the analysis (e.g., Sr-89/90, Total Radium, Total Uranium). The program will offer a menu of options, including data entry, data reporting, and QC reporting

4.3.5.2 For new data, choose data entry. The program will prompt for the name of the file containing the raw data from the counting process. Enter the filename used during data collection as described in section 4.3.3.5 above. The program will import the raw data into a database and query the operator for confirmation of all of the raw data.

STANDARD OPERATING PROCEDURE

TITLE: *GAS FLOW PROPORTIONAL COUNTER - ANALYSIS OF ALPHA AND BETA EMITTING RADIONUCLIDES*

FORM NO.:NONE

4.3.6 Data Reporting

4.3.6.1 In the Windows main menu choose the data reporting option appropriate to the analysis (e.g.,Sr-89/90, Total Radium, Total Uranium). The program will offer a menu of options, including data entry, data reporting, and QC reporting.

4.3.6.2 To report data previously entered into the database, choose data reporting. The program will query for the samples' work order number and which sample numbers to report. The program will prompt to confirm client name, client project ID, and offer up to three 65 character lines of remarks. Enter remarks to note which samples were analyzed as duplicates, shared blank samples, or other simple pertinent information. More detailed information regarding the analysis of the samples should be included on a separate page as a case narrative .

4.3.6.3 To report QC data, choose "QA reporting" from the program menu. Enter the work order number for the report. The program will confirm client name, client project, blank spike or matrix spike values, and offer up to three 65 character lines of remarks. Enter remarks to note blank spike or matrix spike duplicates or multiple work orders which share the QC analyses. Analysis comments of a more detailed nature should be included on a separate page as a case narrative.

5.0 QA/QC

5.1 CALIBRATION PROCEDURES

Refer to ATI SOP770FC0 for calibration procedure.

5.2 QC MONITORING

5.2.1 Quality Assurance and Quality Control practices will be performed in accordance with the procedures set forth in ATI's Environmental Radiochemistry Laboratory QA Manual.

5.2.2 Daily instrument checks will be performed to ensure instrument performance is within proper control limits (See ATI SOP770FC0).

STANDARD OPERATING PROCEDURE

TITLE: *GAS FLOW PROPORTIONAL COUNTER - ANALYSIS OF ALPHA AND BETA EMITTING RADIONUCLIDES*

FORM NO.:NONE

6.0 SAFETY, HAZARDS, AND WASTE DISPOSAL

6.1 SAFETY

Normal laboratory safety procedures must be complied with during the conduct of this procedure. No special safety requirements are mandated by this procedure.

6.2 HAZARDS

Bias applied to detectors is typically in the range of 1500 volts DC. This can result in electric shock if bias cables are disconnected while bias is applied. To minimize the possibility of electric shock, bias will be turned off to any detector before any cabling is disconnected.

6.3 WASTE DISPOSAL

Samples or sample wastes containing radioactive materials which are not being returned to the client must be disposed of according to ATI's procedures for disposal of radioactive materials. Contact the site Radiological Safety Officer for more information. No waste is generated as a direct use of this SOP.

7.0 REFERENCES

7.1 LB4100 Instruction Manual, Oxford Instruments, Inc., Rev. 9/90.

STANDARD OPERATING PROCEDURES

TITLE: ACTINIDES - URANIUM AND PLUTONIUM SEQUENTIAL SEPARATION BY ANION EXCHANGE

FORMS: NONE

PREPARED BY: Tony Vargees
APPROVED BY: TECHNICAL MANAGER _____ DATE 9/26/96
QA/QC OFFICER _____ DATE 1 Oct 96

HISTORY: Rev 0, 7/10/95, PCN #506; *Rev. 1, 9/28/95, PCN #535; Rev. 2, 9/25/96*

1.0 SUMMARY, SCOPE AND APPLICATION

1.1 SCOPE AND APPLICATION

This procedure describes the sequential separation and purification of uranium (U) and/or plutonium (Pu) using anion exchange and the mounting of these analytes for quantitation by alpha spectroscopy. Before using this procedure, an aqueous or solid sample must be prepared as described in one of the appropriate sample preparation SOPs.

At the conclusion of the prep procedures, U and Pu are coprecipitated with ferric hydroxide.

1.2 SUMMARY

The ferric hydroxide precipitate from previous dissolution SOPs is dissolved in hydrochloric acid. The sample solution is passed through a column containing anion exchange resin that is equilibrated in 9N HCl. U and Pu are held by the resin while other sample constituents pass through. The resin is washed with 9N HCl to complete the isolation of U and Pu from the sample matrix. Pu is selectively stripped from the column by washing with 9N HCl / NH_4I solution. Finally, U is stripped by washing the resin with 0.5N HCl. The purified U and Pu are coprecipitated with lanthanum fluoride and mounted on a filter membrane for quantitation by alpha spectroscopy. Either of the two elements, Pu or U, can be isolated using this procedure. The final steps of collecting rinses from the column are ignored if that respective element is not to be isolated for analysis.

2.0 COMMENTS

2.1 Pu can exist in several different oxidation states in aqueous solutions. Pu must be present as Pu(IV) to be successfully purified by anion exchange as described in this procedure. It is essential that as little time as possible elapse between the addition of $NaNO_2$ (in dissolution/concentration procedures) and completion of the anion exchange process.

STANDARD OPERATING PROCEDURES
TITLE: ACTINIDES - URANIUM AND PLUTONIUM SEQUENTIAL SEPARATION BY ANION EXCHANGE
FORMS: NONE

2.2 In 9N HCl, U and Pu(IV) form negatively charged complexes (anions) with Cl^- ions. Therefore, in 9N HCl, U and Pu(IV) are retained by the anion exchange resin. In 9N HCl / NH_4I, Pu(IV) is reduced to Pu(III) which does not form the anionic complex. Hence, when the anion exchange column is washed with 9N HCl / NH_4I, Pu is eluted while U is held. The subsequent washing of the column with 0.5N HCl breaks the U chloride complex and the U elutes from the column.

3.0 REAGENTS AND APPARATUS

3.1 REAGENTS

3.1.1 Hydrochloric acid, HCl, conc. (12N) 9N, 1N, 0.5N:
9N HCl: Cautiously add 1500 mL conc. reagent grade HCl to 500 mL DI water. Dilute to 2 L with DI water.
1N HCl: Cautiously add 150 mL conc. reagent grade HCl to 1650 mL DI water. Mix and allow to cool.
0.5N HCl: Cautiously add 75 mL conc. reagent grade HCl to 1725 mL DI water. Mix and allow to cool.

3.1.2 Hydrofluoric acid, HF., 3N: Dilute 104 mL conc. reagent grade HF to 1 L with DI water. Use plastic graduated cylinder and storage bottle.

3.1.3 Ammonium Iodide, NH_4I, reagent grade.

3.1.4 Titanium Trichloride, $TiCl_3$, 20% solution, reagent grade.

3.1.5 Anion exchange resin, AG 1x8, Eichrome or equivalent, AG 1x2 Bio-Rad or equivalent.

3.1.6 Lanthanum carrier: 0.1 mg La^{3+}/mL: Dissolve 0.078 g high purity $La(NO_3)_2 \bullet 6H_2O$ in 250 mL of 1N HCl.

3.1.7 HCl / NH_4I, 0.73 grams of NH_4I, reagent grade, in 100 mL 9N HCl.

3.1.8 HNO_3 , conc., reagent grade

3.1.9 Safrinine, 1% stock solution, reagent grade.

3.1.10 Polyethylene glycol, average molecular weight 2000 g/mol(PEG 2000) (0.25 M): Dissolve 50 g in 40 ml of DI water and dilute to 100 ml with DI water.

STANDARD OPERATING PROCEDURES
TITLE: ACTINIDES - URANIUM AND PLUTONIUM SEQUENTIAL SEPARATION BY ANION EXCHANGE
FORMS: NONE

Allow the first rinse to pass completely through the column before adding the second rinse. If Am is to be analyzed, collect the first two rinses in the "Am" beaker. Rinse the column with a third 20 mL volume of 9N HCl. Repeat the rinse fourth time. Discard the column effluent from the third and fourth rinses down the drain with plenty of water unless otherwise specified.

4.1.9 If the samples are being analyzed for plutonium, collect the column effluent from this step in a 250 mL plastic cup labeled with the sample ID and the symbol "Pu".

Rinse the resin three times with a 20 mLs of 9 N HCl / NH_4I. (Allow each rinse to pass completely through the column before adding the next.) Collect all three rinses in a 250 ml plastic cup labeled "Pu" with ID number.

4.1.10 Add 1 mL of conc. HNO_3 and heat the solution, **containing the Pu**, to dryness on a hot plate or steam bath. Reduce the heat of the hotplate when the samples are near dryness so that the analyte stays in a soluble form.

4.1.11 If analyzing for uranium, strip the U by rinsing the resin two times with 20 mL volumes of 0.5N HCl. Allow the first rinse to pass completely through the column before adding the second rinse. Collect the column effluent in a 250 mL plastic disposable cup, or other suitable container, labeled with the sample ID and the symbol "U".

4.1.12 Evaporate the solution to dryness by heating on a hot plate or steam bath.

4.1.13 Rinse the column with DI water and discard into the appropriate waste container.

STANDARD OPERATING PROCEDURES

TITLE: ACTINIDES - URANIUM AND PLUTONIUM SEQUENTIAL SEPARATION BY ANION EXCHANGE

FORMS: NONE

4.2 PLUTONIUM MICRO-PRECIPITATION

4.2.1 Add 1 mL conc. HCl to the sample beaker from step 4.1.10. Mix well to resolubilize the dried sample. Place the plastic cup on a steambath for few minutes. Add 14 ml of DI water and mix well.

4.2.2 Add 0.5 mL lanthanum carrier and *0.5 mL of* H_2O_2 . Mix well. Add 5 mL 3N HF. Mix well.

4.2.3 Allow sample to stand for 15-20 minutes minimum.

4.2.4 Place a 25 mm filter membrane on the support screen that sits on the top of the tapered funnel stem. Lock the funnel stem with 25 mm polysulfone filter funnel using twist lock coupling.

4.2.5 Using suction, rinse with 1-2 mL of alcohol (this will make the filter less hydrophobic). Rinse the funnel with DI water after the alcohol rinse.

4.2.6 Filter the coprecipitated sample through the filter membrane.

4.2.7 Rinse the sample beaker once with 5 mL DI water and add to the filter funnel. After the sample has passed through, rinse the filter with an additional 10-15 mL of DI water.

4.2.8 After filtration, turn the vacuum off. Remove the funnel. Use a "Sharpie" marking pen to place a dot on the outside edge of the filter. Carefully remove the filter membrane with a pair of forceps and place it face up in a pyrex beaker. Dry the filter membrane in a drying oven for about one minute at 100° C.

4.2.9 Mount the filter membrane, **face up**, on a 1.25 inch stainless steel cupped planchet with double-sided adhesive tape.

4.3 URANIUM MICRO-PRECIPITATION

4.3.1 Add 1 mL conc. HCl to the sample beaker from step 4.1.12. Mix well to resolubilize the dried sample. Place the plastic cup on a steambath for few minutes. Add 14 ml of DI water and mix well.

4.3.2 Add 0.5 mL of lanthanum carrier.

STANDARD OPERATING PROCEDURES
TITLE: ACTINIDES - URANIUM AND PLUTONIUM SEQUENTIAL SEPARATION BY ANION EXCHANGE
FORMS: NONE

4.3.3 Add ascorbic acid solution dropwise, with swirling, until any yellow color from remaining ferric iron disappears. Add a few drops extra.

4.3.4 Add 1 drop of the safrinine indicator and mix well to obtain a pink solution.

4.3.5 Add *4-5* drops of $TiCl_3$ and *swirl constantly.* The solution should lose the pink safrinine color and be reasonably colorless. If the safrinine color is still present, add $TiCl_3$, until the color is no longer present. If it requires more than *10 drops*, consult the senior analyst or the Technical Manager for further instruction.

4.3.6 Add 5 mL of 3N HF. Mix well.

4.3.7 Allow sample to stand for 15-20 minutes minimum. If the safrinine color returns during this period, add additional $TiCl_3$ until the solution is again colorless then add a few drops extra.

4.3.8 Place a 25 mm filter membrane on the support screen that sits on the top of the tapered funnel stem. Lock the funnel stem with a 25 mm polysulfone filter funnel using a twist lock coupling. Turn the vacuum on. Rinse with 1-2 mL alcohol. (This will make the filter less hydrophobic.) Rinse further with DI water.

4.3.9 Using suction, filter the coprecipitated sample through the filter membrane.

4.3.10 Rinse the sample beaker once with 5 mL 0.4% sodium hydroxide and add to the filter funnel. After the sample has passed through, rinse the filter with an additional 10-15 mL of DI water.

4.3.11 After filtration, turn the vacuum off. *Remove the funnel. Use a "Sharpie" marker to place a dot on the outside edge of the filter. This helps identify the right side of the filter in case the filter flips during drying in the oven.* Carefully remove the filter membrane with a pair of forceps and place it face up in a pyrex beaker. Dry the filter membrane in a drying oven for about one minute at *approximately* 100° C.

4.3.12 Mount the filter membrane, **face up**, on a 1.25 inch stainless steel planchet with double-sided adhesive tape.

STANDARD OPERATING PROCEDURES

TITLE: ACTINIDES - URANIUM AND PLUTONIUM SEQUENTIAL SEPARATION BY ANION EXCHANGE

FORMS: NONE

5.0 SAFETY, HAZARDS AND WASTE DISPOSAL

5.1 SAFETY AND HAZARDS

5.1.1 Read the appropriate MSDS before preparing standards or using any reagents.

5.1.2 Safety glasses, and lab coats must be worn in the radiochemistry prep labs at all times.

5.1.3 Gloves, safety glasses, and lab coats must be worn when working with any chemicals (*e.*g. standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals.

5.1.4 Any chemicals with a Threshold Limit Value of less than 50 ppm shall be worked with in laboratory fume hood (*e.g.*, solvents and acids).

5.1.5 All non-original containers used to hold reagents (*e.g.* wash bottles or automatic dispenser bottles) shall be labeled at a minimum with: 1) the compound name, 2) NFPA Health, Flammability and Reactivity ratings, and 3) date.

5.1.6 Use extreme care when using hydrofluoric acid (HF). Work only in a fume hood that has adequate ventilation. and personnel safety features. Never inhale or allow skin or clothing to be exposed to HF fumes.

5.1.7 Care should be taken when diluting acids. Always add acids to water, NOT water to acid.

5.2 WASTE DISPOSAL

5.2.1 Wastes that are "corrosive only", such as glacial acetic acid and sulfuric acid waste, are disposed of by discharging into the Paragon Analytics waste water treatment facility. These materials that are "corrosive only" (i.e., have no hazardous components or characteristics other than corrosivity) may be neutralized in the waste treatment facility.

5.2.2 Hydrofluoric acid at any concentration is collected in a labeled waste carboy. This includes any excess HF from dissolution of samples and all solutions remaining from the micro precipitation process. Notify the Waste Disposal Technician for disposal.

STANDARD OPERATING PROCEDURES

TITLE: ACTINIDES - URANIUM AND PLUTONIUM SEQUENTIAL SEPARATION BY ANION EXCHANGE

FORMS: NONE

5.2.3 All acid wastes not containing HF that are generated in ion exchange operations are disposed of to the waste tanks (down the drain) unless otherwise specified due to hazardous constituents.

6.0 REFERENCES

6.1 USDOE, RESL/ID, Procedure AS-5, 1979

6.2 USEPA, EMSL/LV, Isotopic Determination of Plutonium, Uranium, and Thorium in Water, Soil, Air, and Biological Tissue, March 1979

STANDARD OPERATING PROCEDURES

TITLE: ACTINIDES - THORIUM AND PLUTONIUM SEQUENTIAL SEPARATION BY ANION EXCHANGE

FORMS: NONE

PREPARED BY: Antony Vargees

APPROVED BY: TECHNICAL MANAGER _____ DATE 11/8/95

QA/QC OFFICER _____ DATE 11/8/95

HISTORY: Rev 0, 7/10/95, PCN #505; Rev1, 9/8/95, PCN #534;

1.0 SUMMARY, SCOPE AND APPLICATION

1.1 *SCOPE AND APPLICATION*

This procedure describes the sequential separation and purification of thorium (Th) and/or plutonium (Pu) using anion exchange and the mounting of these analytes for quantitation by alpha spectroscopy. Before using this procedure, an aqueous or solid sample must be prepared as described in one of the appropriate sample preparation SOPs.

At the conclusion of the prep procedures, Th and Pu are coprecipitated with ferric hydroxide.

1.2 SUMMARY

The ferric hydroxide precipitate from previous dissolution SOPs is dissolved in nitric acid. The sample solution is passed through a column containing anion exchange resin that is equilibrated in 8N HNO_3. Th and Pu are held by the resin while other sample constituents pass through. The resin is washed with 8N HNO_3 to complete the isolation of Th and Pu from the sample matrix. Th is selectively stripped from the column by washing with 9N HCl. Finally, Pu is stripped by washing the resin with 0.5N HCl. The purified Th and Pu are coprecipitated with lanthanum fluoride and mounted on a filter membrane for quantitation by alpha spectroscopy. Either of the two elements, Pu or Th, can be isolated using this procedure. The final steps of collecting rinses from the column are ignored if that respective element is not to be isolated for analysis.

2.0 COMMENTS

2.1 Pu can exist in several different oxidation states in aqueous solutions. Pu must be present as Pu(IV) to be successfully purified by anion exchange as described in this procedure. It is essential that as little time as possible elapse between the addition of $NaNO_2$ (in dissolution/concentration procedures) and completion of the anion exchange process.

STANDARD OPERATING PROCEDURES
TITLE: ACTINIDES - THORIUM AND PLUTONIUM SEQUENTIAL SEPARATION BY ANION EXCHANGE
FORMS: NONE

2.2 In 8N HNO_3, Th and Pu(IV) form negatively charged complexes (anions) with NO_3^- ions. Therefore, in 8N HNO_3 Th and Pu(IV) are retained by the anion exchange resin. In 9N HCl, Pu(IV) forms negatively charged complexes with Cl^- ions but Th does not. Hence, when the anion exchange column is washed with 9N HCl, Pu is held by the resin but Th comes off.

3.0 REAGENTS AND APPARATUS

3.1 REAGENTS

3.1.1 Nitric acid, HNO_3, 8N: Cautiously add 1000 mL conc. reagent grade HNO_3 to 900 mL DI water. Dilute to 2 L with DI water.

3.1.2 Hydrochloric acid, HCl, 9N, 1N, 0.5N:
9N HCl: Cautiously add 1500 mL conc. reagent grade HCl to 500 mL DI water. Dilute to 2 L with DI water.
1N HCl: Cautiously add *166* mL conc. reagent grade HCl to *1834* mL DI water. Mix and allow to cool.
0.5N HCl: Cautiously add *84* mL conc. reagent grade HCl to *1916* mL DI water. Mix and allow to cool.

3.1.3 Hydrofluoric acid, HF., 3N: Dilute 104 mL conc. reagent grade HF to 1 L with DI water. Use plastic graduated cylinder and storage bottle.

3.1.4 Hydrogen peroxide, H_2O_2, 30% reagent grade.

3.1.5 Anion exchange resin, AG 1x8, Bio-Rad or equivalent.

3.1.6 Lanthanum carrier: 0.1 mg La^{3+}/mL: Dissolve 0.078 g high purity $La(NO_3)_3 6H_2O$ in 250 mL of 1N HCl.

3.1.7 Safrinine, 1% stock solution, reagent grade

3.2 APPARATUS

3.2.1 Ion exchange columns, disposable or glass
3.2.2 Filter paper, Whatman 41 or equivalent
3.2.3 Plastic funnel
3.2.4 Glass beads, 3 mm diameter, solid
3.2.5 Suction filter apparatus for 25 mm membrane
3.2.6 Filter membrane

STANDARD OPERATING PROCEDURES

TITLE: ACTINIDES - THORIUM AND PLUTONIUM SEQUENTIAL SEPARATION BY ANION EXCHANGE

FORMS: NONE

3.2.7 Stainless steel cupped planchet, 1.25 inch diameter
3.2.8 Drying oven
3.2.9 Pipets, Eppendorf or equivalent
3.2.10 Wash bottles
3.2.11 Graduated cylinder, plastic, 25 mL
3.2.12 Vortex mixer
3.2.13 Centrifuge bottles, 250 mL disposable, conical
3.2.14 Hot plate
3.2.15 Steam bath
3.2.16 Fine tipped tweezers
3.2.17 Double sided tape
3.2.18 pH paper

4.0 PROCEDURE

4.1 PURIFICATION BY ANION EXCHANGE

4.1.1 Estimate the volume of the ferric hydroxide precipitate in the bottom of the conical 250 mL centrifuge bottle. To dissolve the precipitate, add an equal volume of conc. HNO_3 and mix by vortexing. Add 8 N HNO_3 to bring solution to *50* mL final volume.

4.1.2 Fill a disposable plastic column (approximately 15mm I.D., 18 mL capacity) with AG 1x8 anion exchange resin to a settled depth of approximately 7 cm. Cover the top of the resin bed with glass beads to a depth of approx. 2 cm.

4.1.3 Condition the resin with 50 mL of 8 N HNO_3. Discard the effluent.

4.1.4 Place a fitted plastic funnel on top of the ion exchange column. Fold a Whatman 41 filter paper and place it inside the funnel. Wet the filter paper with 8N HNO_3.

4.1.5 Load the sample solution onto the column through the filter. Pour the sample into the filter in portions *if the volume is more than 100 mL* until the entire solution has passed through the filter and the resin bed. If any other actinides are to be analyzed, collect the effluent in a beaker labelled with the sample ID and the elements to be further separated (e.g., "Am", "U"). Otherwise, discard the column effluent into the appropriate waste container.

STANDARD OPERATING PROCEDURES

TITLE: ACTINIDES - THORIUM AND PLUTONIUM SEQUENTIAL SEPARATION BY ANION EXCHANGE

FORMS: NONE

4.1.6 Rinse the centrifuge bottle two times with 25 mL volumes of 8 N HNO_3. Add the first rinse to the filter (and column). After the solution has passed through the column, discard the filter. (Rinsing the filter in a beaker of water is a convenient way to dilute the acid on the filter prior to disposal.) Allow the first rinse to pass completely through the column before adding the second rinse. If further radionuclides are to be determined, collect the two rinses in the labelled container.

4.1.7 Rinse the column with a third 25 mL volume of 8 N HNO_3. Discard the column effluent down the drain with plenty of water unless otherwise specified.

4.1.8 Rinse the resin three times with 20 mL volumes of 9 N HCl. Allow each rinse to pass completely through the column before adding the second rinse. If the samples are being analyzed for thorium collect the column effluent in a beaker, or other suitable container, labeled with the sample ID and the symbol "Th".

4.1.9 Heat the solution, containing the Th, to dryness on a hot plate or steam bath. Reduce the heat when the samples are near dryness so that the analyte stays in a soluble form.

4.1.10 If analyzing for plutonium strip the Pu by rinsing the resin two times with 20 mL volumes of 0.5N HCl. Allow the first rinse to pass completely through the column before adding the second rinse. Collect the column effluent in a beaker, or other suitable container, labeled with the sample ID and the symbol "Pu".

4.1.11 Take the solution to dryness by heating on a hot plate or steam bath.

4.2 THORIUM MICRO-PRECIPITATION

4.2.1 Add 15 mL 1N HCl to the sample beaker from Section 4.1.9. Mix well to resolubilize the dried sample.

4.2.2 Add 0.5 mL lanthanum carrier. Mix well. Add 5 mL 3N HF. Mix well.

STANDARD OPERATING PROCEDURES
TITLE: ACTINIDES - THORIUM AND PLUTONIUM SEQUENTIAL SEPARATION BY ANION EXCHANGE
FORMS: NONE

4.2.3 Allow sample to stand for 15-20 minutes minimum.

4.2.4 Place a 25 mm filter membrane in a filter funnel assembly and turn the vacuum on. Rinse with 1-2 mL alcohol. (This will make the filter less hydrophobic.)

4.2.5 Using suction, filter the coprecipitated sample through the filter membrane.

4.2.6 Rinse the sample beaker once with 5 mL DI water and add to the filter funnel. After the sample has passed through, rinse the filter with an additional 10-15 mL of DI water.

4.2.7 After filtration, turn the vacuum off. *Remove the funnel. Use a "Sharpie" marker to print a mark on the edge of the filter. This helps identify the right side of the filter in case the filter flips during drying in the oven.* Carefully remove the filter membrane with a pair of forceps and place it face up in a pyrex beaker. Dry the filter membrane in a drying oven for about one minute at *approximately* 100° C.

4.2.8 Mount the filter membrane, **face up,** on a 1.25 inch stainless steel planchet with double-sided adhesive tape.

4.3 PLUTONIUM MICRO-PRECIPITATION

4.3.1 Add 15 mL 1N HCl to the sample beaker from step 4.1.11. Mix well to solubilize the dried sample.

4.3.2 Add approximately 0.5 mL of H_2O_2 and swirl gently.

4.3.3 Add 0.5 mL lanthanum carrier. Mix well. Add 5 mL 3N HF. Mix well.

4.3.4 Allow sample to stand for 15-20 minutes.

4.3.5 Place a 25 mm filter membrane in a filter funnel assembly and turn the vacuum on. Rinse with1-2 mL alcohol. (This will make the filter less hydrophobic.)

STANDARD OPERATING PROCEDURES
TITLE: ACTINIDES - THORIUM AND PLUTONIUM SEQUENTIAL SEPARATION BY ANION EXCHANGE
FORMS: NONE

4.3.6 Using suction, filter the coprecipitated sample through the filter membrane.

4.3.7 Rinse the sample beaker once with 5 mL DI water and add to the filter funnel. After the sample has passed through, rinse the filter with an additional 10-15 mL of DI water.

4.3.8 After filtration, turn the vacuum off. *Remove the funnel. Use a "Sharpie" marker to print a mark on the edge of the filter. This helps identify the right side of the filter in case the filter flips during drying in the oven.* Carefully remove the filter membrane with a pair of forceps and place it face up in a pyrex beaker. Dry the filter membrane in a drying oven for about one minute at *approximately* 100° C.

4.3.9 Mount the filter membrane, **face up**, *(side with the mark)* on a 1.25 inch stainless steel cupped planchet with double-sided adhesive tape.

5.0 SAFETY, HAZARDS AND WASTE DISPOSAL

5.1 SAFETY AND HAZARDS

5.1.1 Read the appropriate MSDS before preparing standards or using any reagents.

5.1.2 Safety glasses, and lab coats must be worn in the radiochemistry prep labs at all times.

5.1.3 Gloves, safety glasses, and lab coats must be worn when working with any chemicals (*eg*. standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals.

5.1.4 Any chemicals with a Threshold Limit Value of less than 50 ppm shall be worked with in laboratory fume hood (*eg*, solvents and acids).

5.1.5 All non-original containers used to hold reagents (*eg* wash bottles or automatic dispenser bottles) shall be labeled at a minimum with: 1) the compound name, 2) NFPA Health, Flammability and Reactivity ratings, and 3) date.

STANDARD OPERATING PROCEDURES
TITLE: ACTINIDES - THORIUM AND PLUTONIUM SEQUENTIAL SEPARATION BY ANION EXCHANGE
FORMS: NONE

5.1.6 Use extreme care when using hydrofluoric acid (HF). Work only in a fume hood that has adequate ventilation. and personnel safety features. Never inhale or allow skin or clothing to be exposed to HF fumes.

5.1.7 Care should be taken when diluting acids. Always add acids to water, NOT water to acid.

5.2 WASTE DISPOSAL

5.2.1 Wastes that are "corrosive only", such as glacial acetic acid and sulfuric acid waste, are disposed of by discharging into the ATI waste water treatment facility. These materials that are "corrosive only" (ie., have no hazardous components or characteristics other than corrosivity) may be neutralized in the waste treatment facility.

5.2.2 Hydrofluoric acid at any concentration is collected in a labeled waste carboy. This includes any excess HF from dissolution of samples and all solutions remaining from the micro precipitation process. Notify the Waste Disposal Technician for disposal.

5.2.3 All acid wastes not containing HF that are generated in ion exchange operations are disposed of to the waste tanks (down the drain) unless otherwise specified due to hazardous constituents.

6.0 REFERENCES

6.1 USDOE, RESL/ID, Procedure AS-5, 1979

6.2 USEPA, EMSL/LV, Isotopic Determination of Plutonium, Uranium, and Thorium in Water, Soil, Air, and Biological Tissue, March 1979

PARAGON ANALYTICS, INC.
STANDARD OPERATING PROCEDURE 712FC4

TITLE: DETERMINATION OF TOTAL ALPHA EMITTING ISOTOPES IN DRINKING WATER -- METHOD 903.0

FORMS: NONE

APPROVED: TECHNICAL MANAGER Debra Hudiver **DATE** 03.31.96
QA/QC OFFICER S Woolland **DATE** 4/4/96

HISTORY: Rev 0, 12/9/92; Rev 1, 3/9/94, PCN # 160; Rev 2, 6/2/94, PCN # 233; Rev 3, 2/25/95, PCN # 398; Rev 4, 3/15/96.

1.0 SCOPE AND APPLICATION

1.1 This standard operating procedure (SOP) and the method it references (EPA Method 903.0) are applicable to the measurement of total soluble alpha emitting radio isotopes of radium -- namely radium-223, radium-224 and radium-226 -- in drinking water and other environmental waters. It is primarily a screening method for radium-226.

2.0 SUMMARY

2.1 The radium in the drinking water sample is collected by co-precipitation with barium and lead sulfate, and purified by co-precipitation from EDTA solution. Citric acid is added to the drinking water sample to ensure that complete interchange occurs before the first precipitation step. The final $BaSO_4$ precipitate which includes radium-226, radium-224 and radium-223 is alpha counted to determine the total disintegration rate of the radium isotopes. A radiometric yield is determined by counting a series of blank spikes.

3.0 RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method This demonstration may come in the form of supervisory/training review, precision and accuracy tests or the successful completion of an unknown proficiency evaluation test.

3.3 Final review and sign off of the data are performed by the department supervisor or designee. Initialing and dating the file indicates that this review for precision accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with sample involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4.0 INTERFERENCES

4.1 The presence of significant natural barium in the sample (i.e. over 1.0 ppm) will cause interference by providing a falsely high chemical yield. In these cases a correction can be made by analyzing duplicate samples spiked with Ba-133 tracer. The tracer yield can be used in lieu of the gravimetrically determined chemical yield.

5.0 APPARATUS AND MATERIALS

5.1 Stainless steel counting planchets, 2" diameter

5.2 Electric stirring hot plate

5.3 Drying oven and/or drying lamp

5.4 Desiccator

5.5 Analytical balance

5.6 Centrifuge

5.7 Glassware

5.8 Hot Water Bath, (90-100 °C)

5.9 a gas-flow proportional alpha particle counting system with low background (< 1 cpm) .

6.0 REAGENTS

6.1 Acetic acid, 17.4N: glacial CH_3COOH (conc.), sp.gr. 1.05, 99.8 percent, ACS reagent grade.

6.2 Ammonium Sulfate, 200 mg/mL: Dissolve 20 g reagent grade $(NH_4)_2SO_4$ in a minimum of water and dilute to 100 mL. Prepare in one liter batches.

6.3 Barium carrier, 16 mg/mL, standardized: Dissolve 2.846g $BaCl_2.2H_2O$ in water, add 0.5 mL 16N HNO_3, and dilute to 100 mL with water. Prepare in one liter batches. Document the preparation of this carrier in the Reagent Prep Logbook.

6.3.1 Standardization of Ba Carrier

6.3.1.1 Add 100 mL DI water to a 250 mL beaker. Prepare a minimum of three (3) replicates.

6.3.1.2 Add stir bar and set at moderate speed.

6.3.1.3 Add one (1) drop non-ionic surfactant and 5 mL Ba Carrier.

6.3.1.4 Add 3 to 5 drops Methyl Red Indicator and acidify with 1:1 HCL until color turns pink then add 2 more mL.

6.3.1.5 Heat to gentle boil and add 5 mL 18 N H_2SO_4 .

6.3.1.6 Maintain heat for 10 minutes, cool and remove stir bar while rinsing with DI water.. Allow to cool..

6.3.1.7 For each of the three beakers tare a 47 mm glass fiber filter in a 2 inch stainless steel planchet on an analytical balance.

6.3.1.8 Record the tare weight.

6.3.1.9 Set up a 1 L vacuum flask with fritted-glass filter support base.

6.3.1.10 Place the filter on the support base and clamp on a glass funnel.

6.3.1.11 Filter the solution, collecting the precipitate on the filter.

6.3.1.12 Wash the filter with 10 mL ethanol using a wash bottle.

6.3.1.13 Transfer the filter gently to the stainless steel planchet.

6.3.1.14 Place the planchet in a petri dish with the lid placed on crooked to allow air into the planchet. Allow the filter to sir dry for a minimum of two hours.

6.3.1.15 Reweigh the filter and planchet. This value will be the gross weight.

6.3.1.16 The recovery of BaSO4 in mg from a 5 mL aliquot will be the difference between the gross weight (planchet, filter, and BaSO4) and the tare weight (planchet and filter). Perform this calculation for all three planchets and average the results.

BaSO4 (mg) = Gross Weight - Tare Weight x 1,000

NOTE: *The calculated average recovery will be used as the 100% value for sample recovery calculations..*

6.4 Citric acid, 1M: Dissolve 19.2 g reagent grade $C_6H_8O_7.H_20$ in water and dilute to 100 mL. Prepare in one liter batches.

6.5 EDTA reagent, basic, (0.25M) reagent grade: Dissolve 20 g reagent grade NaOH in 750 mL water, heat and slowly add 93 g disodium ethylenedinitriloacetate dihydrate ($Na_2C_{10}H_{14}O_8N_2.2H_2O$. Heat and stir until dissolved. Filter through course filter paper and dilute to one liter.

6.6 Lead carrier, 15 mg/mL: Dissolve 2.4 g reagent grade $Pb(NO_3)_2$ in water. Add 0.5 mL 16N HNO_3 and dilute to 100 mL with water. Prepare in one liter batches.

6.7 Sodium hydroxide, 6N: Dissolve 24 g reagent grade NaOH in 80 mL water and dilute to 100 mL. Prepare in one liter batches.

6.8 Sulfuric acid, 18N: Cautiously mix one volume reagent grade 36N H_2SO_4 (conc.) with one volume of water.

6.8 Sulfuric acid, 0.1N: Mix one volume 18N H_2SO_4 (from Section 6.8) with 179 volumes of water.

6.9 Non-Ionic Surfactant

7.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 A representative sample must be collected from a free-flowing source of water and sufficient volume be collected so that adequate aliquots may be taken in order to meet the required MDA

7.2 It is recommended that samples be preserved at the time of collection by adding enough 1 N HNO_3 to effect a pH of 2 (15 mL 1 N HNO_3 per liter of sample is usually sufficient). If samples are to be collected without preservation, they should be brought to the laboratory within 5 days, then preserved and held in the original container for a minimum of 16 hours before analysis or transfer of the sample.

7.3 The sample should be collected in a plastic container.

7.4 The holding time, as defined by the laboratory, is 180 days from collection.

8.0 PROCEDURE

8.1 Preparation of Sample

8.1.1 Filter sample through qualitative paper if suspended solids are present.

8.1.2 To a 1000 mL sample, add 1 to 2 drops non-ionic surfactant, add 5 mL 1M citric acid, 1 mL lead carrier, and 2.0 mL barium carrier. Record the actual volume of sample in mL's on the benchsheet. Use a Class A pipet or calibrated micropipet to deliver the Barium carrier. Record volume and Reagent ID on the benchsheet.

8.1.3 Stir and heat to boiling.

8.1.4 Slowly add 20 mL 18N H_2SO_4.

8.1.5 Digest ten minutes. Remove from heat and retrieve stir bar, rinsing with 0.1 N H_2SO_4.

8.1.6 Cover and let stand overnight.

8.1.7 Aspirate the supernatant. Transfer the precipitate to a centrifuge tube, rinsing the beaker with 0.1 N H_2SO_4.

8.1.8 Centrifuge at 3000 rpm for fifteen minutes. Discard the supernatant.

8.1.9 Wash the precipitate with 0.1 N H_2SO_4. Centrifuge as above and discard wash.

NOTE: The following steps must be completed through Sections 8.1.9 without stopping.

8.1.10 Dissolve the precipitate by adding 15 mL basic EDTA reagent. Heat in a hot water bath and add approximately 1 mL of 6 N NaOH or until solution is complete.

8.1.11 Add 1 mL ammonium sulfate solution and stir thoroughly with a glass rod. Add glacial acetic acid dropwise until precipitation begins. Then add an additional 2 mL of glacial acetic acid. Mix with Vortex mixer or equivalent. Digest in the hot water bath ten minutes. Note the time and date of this precipitation on the benchsheet.

8.1.12 Centrifuge and discard the supernatant into the Pb waste container. Wash the precipitate with 15 mL water. Discard wash.

8.1.13 Transfer precipitate to a tared stainless steel planchet with a minimum of D.I. water. (Tare on an analytical balance to nearest ± 0.1 mg.)

8.1.14 Dry under an infrared lamp or on a hot plate using moderate heat.

8.1.15 Cool to ambient temperature.

8.1.16 Weigh to nearest ± 0.1 mg on an analytical balance. Record weight on benchsheet. Calculate total weight of solids on the planchet in mg and record on the benchsheet. Store planchet in the desiccator until ready for counting.

8.1.17 Count in a gas-flow proportional counter.

8.2 Calibration

8.2.1 The counting efficiency for radium alpha particles with barium sulfate carrier present is determined using a standard (know) radium alpha activity and 32 mg of barium carrier as $BaSO_4$ (same carrier amount used with samples). This is done with spiked distilled water samples and the procedure for regular samples is followed. Note the time of the Ra-$BaSO_4$ precipitation.

8.2.2 The radium-alpha counting efficiency, E, is calculated as follows:

E (cpm/dpm) = C / A x I

where:

C = sample net cpm (gross counts minus background divided by the counting time in minutes)

A = dpm of radium-226 added to sample

I = ingrowth factor for the elapsed time from Ra-$BaSO_4$ precipitation to mid-pint of counting time.

8.3 Calculations

8.3.1 Calculate the radium-226 concentration, D (which would include any radium-224 and radium-223 that is present) in picocuries per liter as follows:

D = C / (2.22 x EVR x I)

where:

C = net count rate, cpm
E = counter efficiency for radium-226 in $BaSO_4$ predetermined for this procedure
V = liters of sample used
R = fractional chemical yield (If R > 1.00, use 1.00)
I = ingrowth correction factor given in equation:

I = 1 + (3 x (1-(exp((-0.693/3.8235) x t))))

2.22 = conversion factor from dpm/pCi

9.0 QUALITY CONTROL

9.1 Prepare a method blank with each batch of field samples. A batch may not contain more than 20 field samples.

9.2 One blank spikes will be prepared with each batch of 20 field samples. Ra-226 will be used as the spike. Refer to the current Spike/Tracer Data Sheet for the amount of spike to use.

9.3 The blank and blank spike will be prepared using one liter of deionized water.

9.4 A sample duplicate will be prepared with each batch at a minimum frequency of five percent (i.e., one in twenty samples) if sample volume is available.

10.0 DEVIATIONS FROM METHOD

10.1 This SOP follows the requirements of Method 903.0. There are no known deviations from the method.

11.0 HEALTH, SAFETY, WASTE

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDS prior to preparing standards or using any solvents or reagents for the first time.

11.1.2 Wear gloves, safety glasses, and lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

11.1.3 Any chemicals with a Threshold Limit Value of less than 50 ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). All flammable compounds must be kept away from ignition sources.

11.1.4 Any non original containers be used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.2 WASTE DISPOSAL

11.2.1 The Total Radium Process Effluent has been determined to not be hazardous except by corrosivity. This material may be discharged into the Waste Water treatment facility.

11.2.2 The total radium analytical process effluent has been determined to not be hazardous in other than corrosivity except the Pb containing supernatant. This supernatant must be segregated into the Pb waste container supplied by the Waste Disposal Coordinator.

6.2.3 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

12.0 REFERENCES

12.1 Prescribed Procedures for Measurement of Radioactivity in Drinking Water, Method 903.0, Alpha-Emitting Radium Isotopes in Drinking Water, EPA-600/4-80-032.

PARAGON ANALYTICS, INC.
STANDARD OPERATING PROCEDURE 702FC10

TITLE: DETERMINATION OF GROSS ALPHA AND GROSS BETA IN WATERS, SOILS, AND AIR FILTERS -- METHOD 9310

FORMS: 702, 720, 302, 631

APPROVED BY: TECHNICAL MANAGER Debbie Henderson DATE 03.28.96

QA/QC OFFICER E Woolland DATE 4/4/96

HISTORY: Rev0, 9/21/92; Rev1; Rev2, 2/25/93, Rev3, 6/17/93; Rev4, 9/20/93, PCN #8; Rev5, 11/4/93, PCN #18; Rev 6, 3/7/94, 3/7/94, PCN #156; Rev 7, 6/7/94, PCN #234; Rev 8, 2/25/95, PCN #399; *Rev 9, 6/20/95, PCN #500; Rev 10, 3/27/96.*

1.0 SCOPE AND APPLICATION

1.1 This standard operating procedure (SOP) and the method it references -- Method 9310 -- describe the procedure used to determine gross alpha and beta activity in soil, air filter, and water samples. Gross alpha and gross beta may be determined simultaneously in the same sample preparation and counting routine. The soil procedure is also amenable to the preparation of suspended solids that have been filtered from aqueous solutions.

1.2 This method provides a rapid screening measurement to indicate whether specific analyses are required. When the gross alpha particle activity exceeds 5 pCi/L, then the same or an equivalent sample shall be analyzed for alpha-emitting radium isotopes (Method 9315) or an alternative measurement of radium-226 alpha emission (Standard Methods for the Examination of Water and Wastewater, 15th edition, Method 705 or 706). Gross beta particle emissions exceeding 15 pCi/L in a sample shall be analyzed for strontium-89 and cesium-134 (Standard Methods for the Examination of Water and Wastewater, 15th edition, Methods 704 and 709). If gross beta activity exceeds 50 pCi/L, then the identity of the major radioactive constituents must be evaluated and the appropriate organ and total body doses determined.

2.0 SUMMARY

2.1 WATERS

The aliquot size is determined for each sample by gravimetric measurement of the total dissolved solids. This aliquot is then evaporated to a small (i.e. < 5 mL) volume and transferred quantitatively into a tared stainless steel (SS) planchet. The planchet is dried on a hot plate and in an oven, then cooled in a desiccator. After cooling, it is weighed to determine the solids deposited. If the weight of solids is > 100 mg a proportionately smaller aliquot must be prepared. Planchets with solids ≤ 100 mg may be sent to the Instrument Group for counting.

2.2 SOILS

A 3 g aliquot of the soil is digested with 30 mL 8N nitric acid in a 50 mL centrifuge tube. The sample is then centrifuged. A volume aliquot which yields < 100 mg of solids is determined gravimetrically. This aliquot is then evaporated onto a tared stainless steel planchet, dried, flamed and weighed. The planchet is then sent to the Instrument Group for counting.

2.3 AIR FILTERS

Air Filters are processed in a manner similar to soils except they need not be weighed and the units are defined as "per filter."

2.4 SUSPENDED SOLIDS

Solids suspended in aqueous solutions are filtered onto tared glass fiber filters. The filters are weighed to determine the weight of the suspended fraction. The entire filtered solid sample, up to 5 grams, is then treated as a soil sample.

3.0 RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method This demonstration may come in the form of supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency evaluation test.

3.3 Final review and sign off of the data are performed by the department supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4.0 INTERFERENCES

4.1 The soil digestion procedure will not completely remove radioactive elements from silica or absorbed radioactive materials will be amenable to this procedure. or other intractable solid matrices.

4.2 This method is applicable to the measurement of alpha emitters having energies above 3.9 MeV and beta emitters having maximum energies above 0.1 MeV.

4.3 The minimum detectable concentration (MDC) to which this method is applicable depends on sample size, counting-system characteristics, background, and counting time.

4.4 In this method for gross alpha and gross beta measurement the radioactivity of the sample is not separated from the solids of the sample. Therefore, the solids concentration is a primary limiting factor in the sensitivity of the method for any given water sample. Also, for samples with very low concentrations of radioactivity, it is essential to analyze as large a sample aliquot as is needed to allow reasonable counting times.

4.5 The largest sample aliquot that should be counted for gross alpha activity is that size aliquot which gives a solids density thickness of $5mg/^{cm2}$ in the counting planchet. For a 2-in. diameter counting planchet (20 cm^2), an aliquot containing 100 mg of nitrated dissolved solids would be the maximum aliquot size for that sample which should be evaporated and counted for gross alpha activity.

4.6 Radionuclides that are volatile under the sample preparation conditions of this method will not be measured. In some areas of the country the nitrated water solids (sample evaporated with nitric acid present) will not remain at a constant weight after being dried at 105° C. Those types of water samples need to be heated to a dull red heat for a few minutes to convert the salts to oxides. Sample weights are then usually sufficiently stable to give consistent counting rates, and a correct counting efficiency can then be assigned. Some radioactivities, such as the cesium radioisotopes, may be lost when samples are heated to a dull red color. Such losses are limitations of the method.

4.7 Moisture absorbed by the sample residue is an interference because it obstructs counting and self-absorption characteristics. If a sample is counted in an internal proportional counter, static charge on the sample residue can cause erratic counting, thereby preventing an accurate count.

4.8 Nonuniformity of the sample residue in the counting planchet interferes with the accuracy and precision of the method.

4.9 Non-aqueous liquid, non-soil solids and samples with high organic content may not be amenable to this procedure

4.10 For the counting of gross beta activity in a water sample, the total solids is not as limiting as for gross alpha activity because beta particles are not stopped in solids as easily as are alpha particles. Very often a single sample aliquot is evaporated and counted for both gross alpha and gross beta activity. In that case, the sample aliquot size would be dictated by the solids limitations for alpha particles.

5.0 APPARATUS AND MATERIALS

5.1 Two-inch stainless steel planchets

5.2 Micro-pipets

5.3 Glassware

5.4 50 mL plastic centrifuge tubes with caps

5.5 Top loading balance ± 0.1 g

5.6 Analytical balance ± 0.1 mg

5.7 Pleated filter paper

5.8 Hot plate

5.9 Wash bottles

5.10 Drying oven

5.11 Graduated cylinders

5.12 Glass Desiccator

5.13 Meeker burner

5.14 Tongs

5.15 Glass rods

5.16 Rubber policeman

5.17 Filtering apparatus for 47 mm filters

5.18 47 mm glass fiber filters

5.19 Centrifuge

5.20 Centrifuge racks

5.21 PC Computer

6.0 REAGENTS

6.1 All chemicals should be reagent grade or equivalent.

6.2 Nitric acid, concentrated (16 N), ACS grade

6.3 Nitric acid, 8 N

6.4 Nitric acid, 1 N

6.5 Distilled or deionized water (Type II) having a resistance value between 0.5 and 2.0 megaohms (2.0 to 5.0 mhos)/cm at 25 'C.

6.6 Silica sand, Aldrich no. 27, 473-9 (-50 to -70 mesh), or equivalent

7.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 All samples must be collected in a manner that addresses the considerations discussed in Chapter Nine of EPA SW-846.

7.2 It is recommended that aqueous samples be preserved at the time of collection by adding enough 1N HNO_3 to the sample to bring it to pH 2 (15 mL 1N HNO_3 per liter of sample is usually sufficient). If aqueous samples are to be collected without preservation, they should be brought to the laboratory within 5 days and then preserved and held in the original container for a minimum of 16 hr before analysis or transfer of the sample. Aqueous samples are collected in 1 liter poly bottles.

7.3 Soils samples are not preserved. It is sufficient to collect a 10-20 g aliquot.

7.4 The container should be plastic rather than glass to prevent loss due to breakage during transportation and handling.

7.5 No holding time is stated in Method 9310.

8.0 PROCEDURE

8.1 CALIBRATION PROCEDURES

8.1.1 Efficiency Calibration

Standards for calibration and Daily *QC* Checks shall be traceable to the National Institute for Standards and Technology (NIST). Standards will normally be of ^{241}Am for alpha and ^{137}Cs or ^{90}Sr for beta. The analysis systems shall be

calibrated for each physical form of sample to be analyzed (e.g., sample evaporated on planchet, filter, etc.) at least annually.

Multiple acquisitions of calibration data are preferred. This data may be obtained by multiple counts of the same sample or by counting several similar samples sequentially. The calibration is performed by first obtaining alpha count information, then beta count information.

8.1.1.1 Place the alpha calibration source(s) on the sample tray and place on the counter directly after the group tray. Place the next group tray after the alpha sample(s), then place the beta calibration source(s) after the second group tray.

8.1.1.2 Start data acquisition by selecting LB5100 from the menu, then choosing Start Count from the submenu. Choose Efficiency_Alpha_Beta from the counting options, then choose the group name associated with the alpha standard(s). Note the file name into which the alpha data will be stored. Repeat this procedure for the beta standard(s), noting the file name for the beta data.

8.1.1.3 When the counts are complete, the data must be matched with the source data stored in the source data file. Choose Data Output from the LB5100 menu, then choose the data file in which the alpha information is stored. The calibration data file is offered, with a blank box for the standard ID. Enter the standard ID for the alpha sample(s), normally 1003 for the's 100μl Am-241 standards and 1001 for the's 100μl Cs-137 standards. The spreadsheet will calculate the efficiency for the appropriate measurement(s). The beta efficiency should be approximately 50%, and the alpha efficiency should be approximately 28%. If the efficiency data is valid, press Archive to store the data. If this is an initial or scheduled calibration, press ***Mean*** to store the efficiency data for use by all subsequent analyses. If this is a routine efficiency check, press ***Daily*** to add the data to the efficiency control chart. Repeat this procedure such that both alpha and beta efficiency data are stored.

8.1.2 Attenuation Calibration

Alpha emitting samples which contain any measurable mass deposited on the planchet must be corrected for alpha particle attenuation. This correction is then applied to the sample during the analysis phase.

Multiple acquisitions of attenuation data are required. This data is obtained by creating multiple alpha standards of the same activity and varying masses, normally 0 to 200 mg. Each sample is counted and a fitted curve is generated to the attenuation data.

8.1.2.1 Place the alpha attenuation sources on the sample trays and place on the counter directly after the group tray.

8.1.2.2 Start data acquisition by selecting LB5100 from the menu, then choose ***Start Count*** from the submenu. Choose Attenuation_Alpha_Beta from the counting options, then choose the group name associated with the alpha standards. Note the file name into which the alpha attenuation data will be stored.

8.1.2.3 When the counts are complete, the data must be matched with the known data for the standards. Choose Data Output from the LB5100 menu, then choose the data file in which the alpha attenuation information is stored. The attenuation calibration data file is offered. Enter the mass information for the samples. The spreadsheet will calculate the attenuation curves. Press Archive to store the data. The attenuation data will be used in all future required applications.

8.2 PROCEDURE FOR WATERS

8.2.1 Verify with pH paper that the sample has been properly preserved to a pH <2. Record the pH on the sample condition form. (FRM631)

8.2.1.1 If the pH is ≥ 2, acidify to <2 with concentrated HNO_3. Shake, wait for two (2) minutes and retest pH. Record the acid addition and the final pH on the Sample Condition form. Note also the date and time of acidification.

8.2.1.2 Return the sample to storage for at least 16 hours before proceeding. Record the beginning date and time on a Sample Condition Form. If sixteen (16) hours causes a scheduling difficulty, notify the Project Manager to determine if a deviation from this requirement is acceptable. Document any deviations thoroughly on a QA Summary Sheet that accompanies the project file.

8.2.1.3 When resuming the analysis, record the date/time of resumption on the Sample Condition form. Also, calculate and record the number of elapsed hours since acidification.

8.2.2 Consult the sample prescreen data (if any) to find the weight (W) (in grams) of solids deposited by the 1.0 or 5.0 mL prescreen aliquot. The sample aliquot size V (in mL) for the gross alpha/beta (A/B) analysis is then calculated for 5 mL aliquots by:

$$(mL) = \frac{0.45}{W(g)} \qquad \textit{Equation}$$

One mL aliquots should use five times the value calculated by Equation 1. Record the value in the sample aliquot column.

8.2.2.1 Prepare an electronic bench sheet by entering the required information on the bench sheet template, and the individual sample ID in the Work Order Number column. Save the created bench sheet under the first work order number in r\opr\radio\bench-sh directory.

8.2.2.2 If gross A/B analysis is requested on a sample that was not prescreened, determine the weight of solids in 10 mL of the sample as follows. Record the necessary information on the Sample Condition form noting "gravimetric aliquot deter'".

8.2.2.3 Label and tare a planchet to nearest 0.1 mg. Enter the reading into the designated cell for that sample in the "Tare PC" column of electronic bench sheet.

8.2.2.4 Shake the sample well and pipet 10.0 mL of sample into the labeled, tared planchet using calibrated or class A glass pipet.

8.2.2.5 Dry on a hot plate. Cool, then reweigh. Enter the reading into the designated cell for that sample in the "Gross PC" column of Gravimetric Aliquot Determination section of the electronic bench sheet.

8.2.2.6 The solid mass and volume aliquot will be calculated using Equation 2, and the results will be shown in the respective cells in the Solid Mass and Calc. Aliq. columns in the Gravimetric Aliquot Determination section of the electronic bench sheet. The Digest Aliquot column shows the Calculated Aliquot plus the 10 mL used for aliquot determination as final aliquot used.

$$(mL) = \frac{0.9}{W(g)} \qquad \textit{Equation 2}$$

8.2.2.7 If the planchet weight is unstable or salts are excessive, flame the 10 mL planchet and recalculate. If that is done, the resultant sample planchet needs to be flamed also.

8.2.3 If the calculated aliquot volume is greater than 1000 mL, use a one liter sample aliquot size.

8.2.4 Measure sample calculated aliquot from well shaken sample into labeled glass beaker. Add concentrated HNO_3 in the ratio of 1/10th the sample volume. (e.g., 100 mL acid per L of sample.)

8.2.5 Evaporate the sample on a hot plate to near dryness (≤1 mL). Add 10 mL concentrated HNO_3, rubbing the sides and bottom with a rubber policeman, and transfer quantitatively to labeled 50 mL or 150 mL beaker. Rinse with small portions of 8 N HNO_3 and add to the beaker. (If original volume was evaporated in a 50 mL or 150 mL beaker, there is no need to transfer to a second beaker).

8.2.6 Slowly evaporate sample solution to 1 to 2 mL on a hot plate. Avoid spattering by reducing the heat on the hot plate. Transfer quantitatively to the same labeled SS planchet used for the 10 mL aliquot determination. Use very small portions of 8 N HNO_3 to rinse beaker, rubbing the sides and bottom with a rubber policeman. Rinse beaker walls at least three times. If planchet cannot hold all rinses, add them as planchet volume is evaporated in the next step.

8.2.7 Evaporate solution in planchets to dryness using a hot plate in a hood. Avoid excess heating that causes spattering or boiling.

8.2.7.1 Flame the planchet if the 10 mL planchet was flamed.

8.2.8 When all planchets are dry remove and put them in oven at 105 °C for at least one hour, then cool the samples in a desiccator.

8.2.9 Remove samples from desiccator and after 15 minutes weigh planchets on an analytical balance. Enter the weight to the nearest 0.1 mg in the designated cell of the Final Gross PC column. The weight in mg of solids in planchet (W') will be calculated in the Final Solid Mass column of the electronic bench sheet.

8.2.9.1 If the weight is > 100 mg, rinse the entire solid mass on the planchet with enough 8N HNO_3 into a tared glass beaker. Weigh the rinsate and

calculate a rinsate aliquot volume (V') by Equation 3 and transfer quantitatively to the same labeled SS planchet used for the 10 mL aliquot determination and return to section 8.2.7. Do not proceed with sample residue weights > 100 mg.

$$'(mL) = \frac{190mg}{w'(mg)}\, v(mL) \qquad \textit{Equation 3}$$

8.2.10 Let planchet stand outside of the desiccator for 15 minutes. Are samples noticeably hygroscopic and have gained weight? If samples are not noticeably hygroscopic, they are ready for counting. But if they are hygroscopic, proceed with Section 8.2.11.

8.2.11 Cautiously flame planchet to dull redness over a Meeker burner. Avoid popping and spattering. Maintain heat for at least one minute. Cool in desiccator. Reweigh to nearest 0.1 mg and reenter the new weight in electronic bench sheet. Samples are ready for counting.

8.3 PROCEDURE FOR SOILS

If Analysis is based on dry weight basis, use oven dried or ground soil samples.
Rocky, coarse or non-homogeneous soils should be milled or ground to pass a No. 4 sieve before taking an aliquot for analysis. See SOP 721FC for the soil preparation procedure.

8.3.1 Weight 3 g of soil sample to the nearest 0.1 g into a labeled 50 mL centrifuge tube.

8.3.2 Add 30 mL 8 N HNO_3

8.3.3 Mix to break up clumps.

8.3.4 Heat in specifically designed steam baths for (1) one hour.
Centrifuge at 3000 rpm for 10 minutes, Filter supernatant using VWR Grade 313 pleated paper, or equivalent, into a new labeled centrifuge tube.

8.3.5 Determine the weight of solution in 5 mL of the solution as in Section 8.2.2. The 5 mL planchet should be flamed for all soil samples. Calculate and record the required aliquot volume of solution as in section 8.2.2. Aliquots should be in increments of 5 up to 20 mL. If the calculated aliquot exceeds 20 mL, use a 20 mL aliquot.

8.3.5.1 If the weight of deposit from the 5 mL aliquot is more than 100 mg calculate the required less than 5 mL filtered aliquot and proceed to

Section 8.2.4. Aliquots should be in increments of 1 mL.

8.3.6 Directly transfer the additional aliquot to the planchet used for the 5 mL aliquot.

8.3.7 When the final transfer is made and planchet is dry, flame planchet gently to a dull red color.

8.3.8 If the residue weight exceeds 100 mg, and not enough digestate is left to dry on a new planchet with recalculated aliquot then proceed as in section 8.2.9.1.

8.4 PROCEDURE FOR SUSPENDED SOLIDS

8.4.1 Label a 2" stainless steel planchet for each sample. Tare with a 47 mm glass fiber filter. Record the tare weights on a Quality Assurance Summary Sheet (QASS), Form 302 FC.

8.4.2 Filter the aqueous sample through the tared glass fiber filter. Return the filter to the labeled planchet.

8.4.3 Reweigh the planchet/filter and record on the QASS.

NOTE: If samples that have been submitted, are already filtered on glass fiber, then the analyst may omit Section 8.4.1 and 8.4.3 and enter the procedure at this point.

8.4.4 Subtract the tare weight in Section 8.4.1 from the gross weight in Section 8.4.3 to determine the weight of suspended solids. If results are requested on a dry weight basis, the filters must be dried overnight prior to re weighing. Samples yielding over 5 grams of suspended material should be scraped down gently with a spatula until the weight is approximately 5 grams. Record the final weight of suspended solids in the sample weight column of the soils benchsheet.

8.4.5 The sample preparation now proceeds as a soil in Section 8.3. The entire filtered sample, including the filter, is transferred to the 250 beaker in section 8.3.1. Submit the QASS with the benchsheet and note in the header of the benchsheet that the analysis is for suspended solids rather than soils.

8.5 CALCULATIONS

8.5.1 Calculate the weight of solid deposit by subtracting the tare weight (g) from the gross weight (g). This gives the solids deposit weight in grams. To convert to mg, multiply the grams by 1000.

8.5.2 WATER

Calculate the alpha and beta activity in pCi/l as follows:

$$Activity\ (pCi/1) = \frac{(Sample\ CPM - Background\ CPM)}{Efficiency * Volume * 2.22\ (DPM/pCi) * (b * m^{x})}$$ Equation 4

where: Sample CPM = the raw sample count rate, obtained from the raw data file

Background CPM = the alpha or beta background count rate, obtained from the analysis report header

b = the attenuation curve offset value, from the raw data file

m = the attenuation curve slope value, from the raw data file

x = the analysis mass in mg

Efficiency = the fractional efficiency for alpha or beta counting, from the analysis report header

Volume = the sample volume in liters, from the analysis report

8.5.3 SOLIDS

Calculate the alpha and beta activity in pCi/g as follows:

$$Act.(pCi/g) = \frac{(Sample\ CPM - Background\ CPM)}{Eff.*Mass*2.22\,(DPM/pCi)*(b*m^{x})} * \frac{FiltrateVolume}{Filtrate\ Aliquot}$$

Equation 5

where: Sample CPM = the raw sample count rate, obtained from the raw data file

Background CPM = the alpha or beta background count rate, obtained from the analysis report header

b = the attenuation curve offset value, from the raw data file

m = the attenuation curve slope value, from the raw data file

x = the analysis mass in mg

Efficiency = the fractional efficiency for alpha or beta counting, from the analysis report header

Mass = the analysis mass in mg, from the analysis report

Filtrate Volume is the volume of acid used for sample digestion, from the bench sheet or report header

Filtrate Aliquot is the aliquot of acid used for sample digestion, from the bench sheet or report header

9.0 QUALITY CONTROL

9.1 Reagent blanks should be run at a frequency of five percent (i.e., one per 20 field samples) with a minimum of one per batch. Reagent blanks for waters shall consist of deionized (DI) water and match the volume used for blank spikes. Reagent blanks for soils shall be 30 mL 8N nitric acid.

9.2 Blank spike samples shall be run at a frequency of five percent with a minimum of one per batch. The activity will be spiked into 28 mL of 8N nitric acid mixture at the start of the procedures. Alpha activity will spike using an Am^{241} standard and beta activity with a Sr-90 standard.

9.2.1 Consult a current copy of the Spike/Tracer Data Sheet, for the identification of the proper Am^{241} and Sr-90 working standards and spike volumes. (Check with Supervisor for current copy, see example attached.)

9.2.2 The volume of DI water used for QC samples in water sample batches may vary from a minimum of 100 mL , up to 1000 mL (in even 100 mL increments) depending on the largest sample volume used in that batch. The QC sample volumes must be no smaller than this volume.

9.3 Replicate samples shall be run at a frequency of ten percent with a minimum of one per batch. Client requested replicate analyses shall be run as required and may count as the QC replicates for that batch.

9.4 Matrix spike samples and spiked duplicate analyses shall be run as requested by the client.

9.5 QC samples must be run to match the matrices in that batch.

9.6 Reagent blanks for air filter and suspended solids samples shall consist of one clean glass fiber filter. Blank spikes for such samples shall consist of one filter which has been spiked with the Am^{241} and Sr-90 working standards.

9.7 Blank spikes for soil samples shall consist of 3 grams of clean silica sand. Spike the activity into the sand at Step 8.3.1 of the soil procedure.

10.0 DEVIATIONS FROM METHOD

10.1 This SOP follows the requirements of Method 9310. Following are two (2) exceptions to Method 9310.

10.1.1 In this procedure, alpha and beta activities are counted simultaneously at the beta plateau. Methods 9310 and 900 instruct the counting of alpha and beta at their respective plateaus. By setting the alpha/beta discriminators such that there is negligible contribution of beta events to the alpha energy region, there is no effective advantage for counting on the respective voltage plateaus. However, there are significant disadvantages to counting on the two plateaus independently. (1)The count time required immediately doubles and (2) the alpha efficiency is significantly lower at the alpha plateau such that count times may need to be increased to reach the required detection limit.

10.1.2 Method 9310 is written for surface and groundwaters. Per the client's request, Paragon Analytics will modify the method as described for soils and air filters.

11.0 HEALTH, SAFETY, WASTE

11.1 SAFETY AND HAZARDS

11.1.1 Safety glasses, lab coats and gloves should be worn in the laboratory at all times.

11.1.2 Use care when handling mineral acids (e.g. HNO_3). Work only in a fume hood with adequate ventilation and wear appropriate eye, face, and body protection.

11.2 WASTE DISPOSAL

11.2.1 The Gross Alpha/Beta analytical process liquid effluent has been determined to not be hazardous in other than corrosivity. This material may discharged into the waste water treatment facility. Here the solution will be neutralized prior to discharge and the activity will be monitored to ensure compliance with Colorado Rules and Regulations pertaining to Radiation Control Part 4 regarding discharges to sanitary discharges to sanitary sewers.

11.2.2 Solids and filtered residues shall be accumulated in a 2 liter wide-mouth Nalgene bottle for further evaluation prior to disposal.

12.0 REFERENCES

12.1 EPA SW-846, Method 9310, Gross Alpha and Gross Beta, Revision 0, September 1986.

12.2 Prescribed Procedures for Measurement of Radioactivity in Drinking Waters, Method 900.0, EPA-600 4-80-032, August 1980.

@ AIR TOXICS LIMITED
STANDARD OPERATING PROCEDURE

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN Summa^{tm} POLISHED CANISTERS

EPA METHOD TO-14

SOP # 6

Effective Date:	1/11/96
Revision #:	7
Reason for Revision:	To Amend Result Calculation Procedures and Clarify Section 5.0

Laboratory Director: Linda L. Freeman — 1/11/96
Linda L. Freeman — Date

Quality Assurance Officer: Isabella C. Crume — 1/11/96
Isabella C. Crume — Date

1.0 PURPOSE

1.1 To provide a procedural guide for the application of EPA Method TO-14 to the analysis of volatile organic compounds in ambient air using evacuated stainless steel summa canister collection. The EPA method is followed without modification.

1.2 To describe specific adaptations of the method to the analysis of the EPA Clean Air Act List of target compounds.

2.0 PROCEDURES

2.1 EPA Method TO-14 describes techniques for the analysis of airborne VOCs collected as whole air samples in stainless steel canisters. One liter of air is withdrawn from the canister through a mass flow controller and cryofocused at -189°C in a dewar of liquid argon. The focused air sample is then flash heated through a hydrophobic drying system which removes water from the sample stream prior to analysis by full scan GC/MS.

2.2 Materials, Supplies and Equipment

25 µL, 500 µL, 1 mL, 2.5 mL, 5 mL and 25 mL gastight syringes (CMS)
Certified NIST Traceable VOC blends - Scott Specialty Gases
Aldrich Chemical High Purity Neat Standards (Lab Certified)
Tedlar Bags (1L, 3L and 10L) SKC
Heating Tapes - Various Lengths (Cole Palmer)
Power Controllers (Cole Palmer)

HP 5970, HP 5971 and HP 5972 MSDs with UNIX Operating System/Thru-Put Software
NIST /NBS54.1K Library Search Software
RTX-624 105 m X 0.53 mm Megabore™column

Liquid Argon 5500 cu. ft. dewar (Local Supplier)
Ultra High Purity Helium (Local Supplier)
Liquid cryogenic dewars (300 mL, 500 mL, 5000 mL) CMS

Laboratory designed cyrofocusing TO-14 interface equipped with six port heated (at ca. 180°C) Valco valve for sampling and backflushing contents of the cryotrap to the drier. The cryotrap consists of 1/8 inch stainless steel tubing packed with acid washed glass beads and wrapped around a cartridge heater (at ca. 175°C). The cryofocusing unit is attached to the drier by a 1/16 inch stainless steel heated transfer line maintained at ca. 65°C. Purge/Desorption Gas flow is regulated by a flow controller on the canister interface. Canisters are connected to the cryofocusing unit

through a 5 micron particulate filter. Optional syringe injection of gaseous standards is accomplished through a Swagelok T equipped with septum cap just prior to the sampling valve.

Laboratory designed drying system which consists of a 1/8 inch packed tube containing a hydrophobic sorbent housed in a heated block. Water passes through the drier at ambient temperature while organic VOCs are retained. Following the drying cycle, the tube is heated to 270°C and the VOCs are backflushed to the GC/MS through a heated fused silica transfer line connected to the packed column injection port.

Tylan Mass Flow Control Module (1 to 100 mls/min. Air)
Edwards Vacuum Pump

Laboratory Designed Heated Dynamic Gas Dilution Manifold - based on Porter flow controllers and Sierra digital flow sensors for calibration and diluent gases

Laboratory Designed Canister Receiving Station equipped with high resolution vacuum/pressure gauge and diluent gas inlet.

2.3 Analysis is carried out on a GC/MS system equipped with a Megabore™ inlet adapter, cryogenic oven controller, a J&W Scientific RTX-624 column and a Hewlett-Packard 5970, 5971 and 5972 Mass Selective Detectors. The detectors are equipped with a jet separators.

2.4 The GC/MS operating conditions include:

Column: 105 m x 0.53mm RTX-624 (Restek)

Injector Temperature: 150°C
Oven ramp: 40°C for 5 min., 5°/min. to 180°C for 3 min.
Carrier Gas: UHP Helium at 15 mLs per min.
Separator Temperature: 220°C
Source Interface Temperature: 250°C

Scan: Low mass 35 amu (29 amu when analyzing for Methanol)
High mass 350 amu
Scan rate: 2 seconds per scan

Drier Purge Time : 8 to 10 minutes
Drier Desorb Preheat Temperature: 240 to 245°C
Drier Desorb Temperature: 250°C
Drier Desorb Time: 3 to 10 minutes
Bake Temperature: 270°C

Bake Time: 8 to 10 minutes
Trap/Drier Carrier Flow: 25 mLs per minute UHP Helium
Note: the drier conditions are optimized for each unit with the above as guidelines.

Canister Interface Valve/Line Temperature: 150°C
Sample Volume: Cryotrap 20 min. @ 50 mL/min. (1 Liter)
Desorption Temperature Cryotrap: 150°C
Desorption Time Cryotrap: 8 min.

2.5 Quantitation is based on the internal standard technique. The internal standards, Bromochloromethane, Chlorobenzene-d5 and 1,4-Difluorobenzene are spiked into each standard, blank, sample and QC sample at 50 ppbv. Also spiked into all standards, blanks, samples and QC samples are three surrogates. The surrogates Octafluorotoluene, Toluene-d8 and 4-Bromofluorobenzene are spiked at 50 ppbv.

3.0 CANISTER MOUNTING AND SPIKING PROCEDURES

3.1 Upon receipt, the canister vacuum/pressure is recorded. Under normal field conditions the canisters will either be at ca. 10"Hg vacuum or ambient pressure. Canister receipt vacuum/pressure is reported on the front page of the data report. If abnormal conditions exist the project contact is notified by the sample custodian or a client services representative before analysis can begin. Data from such samples will be qualified. Prior to analysis, the canister is pressurized to 5 psig for 6 L canisters and 15 psig for 1 L canisters.

3.2 Canisters are connected to the inlet line of the cryofocusing unit with 1/4" stainless steel fittings. Connections are leak checked by monitoring the flow on the Tylan controller. As vacuum is achieved, the flow will drop to zero. After leak checking is complete, the valve on the canister is opened and flow allowed to equilibrate for 1 minute. The equilibration period also allows for sweeping of the line/trap.

3.3 Sampling is initiated by rotating the Valco six port valve into the sample position. Air from the canister flows into the cryotrap which is placed in a dewar of liquid argon. Sampling continues for a period of 20 minutes or until the desired volume of air has been withdrawn. During this time, a 1 cc gas sample valve injection of IS/Surrogates is made.

3.4 Following the 20 minute sampling period, the six port valve is rotated into the backflush position, the Dewar of liquid argon removed and the trap heater turned ON. Contents of the cryotrap are then swept by carrier gas into the drier for a period of 10 minutes. Following this time period, the

drier is flash heated and the contents backflushed into the GC/MS over a 10 minute period of time. A 15 minute bake cycle is then used to clean the system for the next sample. The bake cycle eliminates sample carryover by sweeping both the heated trap and heated drier to vent.

4.0 QUALITATIVE ANALYSIS

4.1 Qualitative Target Compound Identification

4.1.1 An analyte is qualitatively identified when two criteria are met:

1) The Relative Retention Time (RRT) for the analyte must be within +/- 0.06 RRT units of the RRT of the analyte in the daily continuing calibration check.

2) Ions present in the standard spectrum greater than 10% of the most abundant ion must be present. Also, the relative intensity of the ions greater than 10%, must be +/-20% of the intensity in the standard spectrum. The standard spectrum is generated by the system that is performing the analysis. See *Appendix E* for a list of the Quantitation Ions used for each compound.

It may be necessary for the analyst to perform manual background subtraction of coeluting peaks to obtain a clean spectrum. The analyst must always use their discretion on any identification.

4.2 Tentatively Identified Compounds (TIC)

4.2.1 When requested, the analyst searches the ten highest non-target unknown peaks. The spectrum of these peaks are searched against the NIST library of greater than 50,000 compounds. The analyst evaluates the top three library searches to determine the tentative identity of the unknown compound. Based on the computer generated searches, the identification is assigned. The analyst must use their discretion on any identification.

4.2.2 The total ion current is used for quantitation and calculation of TIC results. The total ion current of the closest (by Retention Time) internal standard is used to calculate results. A relative response factor of "1" is assumed.

5.0 CALCULATIONS

Response Factors:

$$\text{Relative Response Factor (RRF)} = \frac{\text{Area of Compound}}{\text{Area of Internal Std.}} \times \frac{\text{Concentration of Int. Std. (ppbv)}}{\text{Concentration of Compound (ppbv)}}$$

Results Calculation:

$$\text{ppbv On Column} = \frac{\text{Area of Compound in Sample}}{\text{Area of Int. Std. in Sample}} \times \frac{\text{Concentration of Int. Std. (ppbv)}}{\text{Continuing Calibration Check's RRF *}}$$

ppbv In Sample = ppbv On Column X Dilution Factor

Note: The dilution factor includes canister pressurization dilution and any subsequent dilution required to ensure all results are within the instrument calibration range.

* The average RRF from the initial calibration curve is used as projects specify.

6.0 QUALITY CONTROL

6.1 Preparation of Standards

6.1.1 Calibration is performed at a minimum of five levels. One standard must be at or near the reporting limit. Standards are prepared from laboratory certified Aldrich neat materials and NIST Traceable Scott Specialty Gas VOC blends. Standards prepared in neat form are first subject to capillary GC/FID analysis to determine purity. The percent purity must be greater than 96% or correction factors are used. Following the purity check, the standards are blended into the working range by taking known aliquots and using density based calculations.

6.1.2 Certified Gas Blends

The original 40 component TO-14 list of analytes is purchased from Scott Specialty Gases (See *Appedix H*) blended to 5 ppmv in a high pressure cylinder. The blend is produced by the manufacturer using criteria designed to minimize vapor phase interactions and maximize long term stability. The high level cylinder is connected to a dynamic dilution manifold as defined in Method TO-14. By adjusting the relative flows on the controller various ppbv level standards are achieved.

6.1.3 Certified Calibration Blend

Adjust the flow controller on Std A to 3 mLs per minute. Adjust the diluent UHP Nitrogen to 150 mLs per minute. Blend into a 10 L Tedlar Bag. Final concentration is 100 ppbv. Alternatively, the certified gas blend is put directly into a 1 L canister for a final concentration of 5 ppmv. Aliquots of this are injected into the system. Standards prepared in a canister in this manner may be used for up to one month from date of preparation. If stored in a Tedlar bag, the standard must be discarded after 3 days.

6.1.4 Laboratory Blends from Neat Materials

Analytes not present in the Scott Gas blends were purchased in neat form from Aldrich Chemical Company. These compounds are blended in the gas phase by attaching a Tedlar bag to the TO-14 blending manifold and filling with UHP N2 to an accurately measured volume of 1, 3 and 10 liters. After the gas has filled the bag, prescribed amounts of the neat material are injected into the bag. Density based calculations are used to determine the prescribed amounts and final concentrations. (Note: Tedlar bags are used for the static dilution medium due to their inherent inertness to polar analytes vs. glass dilution jars. Standards should not however be stored in the Tedlar bags beyond 3 days. Fresh calibration standards are prepared and then transferred in final form to Summa canisters for storage. The standards in Summa Canisters must be discarded after 6 months.)

6.1.5 Neat Materials Calibration Blend

Spike appropriate amounts of neat from *Appendix B* into a 10 L Tedlar Bag filled with 8 L of UHP Nitrogen. The resulting concentration is 100 ppmv. The 100 ppmv standard is drawn into an evacuated 6 L Summa canister. The Summa canister is pressurized from 0 "Hg to 20 psig for a dilution of 1:2.02. The final concentration of the standard is 50 ppmv.

6.1.6 Combined Calibration Blend

The contents of the calibration Tedlar bag described in 6.1.3 are immediately drawn into a 6 L evacuated SUMMA canister for long term storage and stability. Prior to analysis the canister is pressurized to 20 psig resulting in a 50 ppbv calibration stock. Standards prepared in a canister in this manner may be used for up to one month from date of preparation.

6.1.7 Internal Standard/Surrogate Mix

Blend the prescribed amount of neat material into a Tedlar bag to a final volume of 8.0 liters. Transfer the contents of the Tedlar bag to an evacuated Summa canister and pressurize to 20 psig. The final concentration is 50 ppmv. This type of standard may be used for up to 6 months.

	COMPOUND	DENSITY	FW	µL	ppmv
	Bromochloromethane	1.991	129.39	2.9	50
	Chlorobenzene-d5	1.157	117.7	4.8	50
	1,4-Difluorobenzene	1.110	114.09	4.6	50
(Surrogate)	Octafluorotoluene	1.666	136.06	2.7	50
(Surrogate)	Toluene-d8	0.867	100.21	3.8	50

	COMPOUND	DENSITY	FW	µL	ppmv
(Surrogate)	4-Bromofluorobenzene	1.593	175.01	1.5	50

6.2 Five Point Multilevel Calibration

The five point calibration is constructed by loading varying amounts of the Combined Calibration Blend on the canister interface. The standard volume of air withdrawn is one liter, consequently lower loadings result in an effective dilution.

CAL 1	2.0 or 5.0 ppbv *
CAL 2	5.0, 10 or 25 ppbv *
CAL 3	50 ppbv
CAL 4	100 ppbv
CAL 5	200 ppbv

* Some compounds do not respond well and therefore the CAL 1 and CAL 2 points may vary by compound.

Always introduce 1.0 mL of the IS blend described in Section 6.1.7 into the canister interface as each standard or sample is being loaded. The IS amount loaded in this fashion will be 50 ppbv per component.

6.3 BFB Check Mix

Spike 625 µL of certified 2000 µG/mL 4-Bromofluorobenzene (see *Appendix C*) standard into 50 mL of Methanol. The final concentration is 25 µG/mL or 25 nG/µL of 4-Bromofluorobenzene. A 2.0 µL of this standard is injected for the 50 nG on column tune check.

6.4 Calibration and QC Checks

6.4.1 Calibration of the GC/MS is achieved via the internal standard technique. The response factor variability over the 5 point curve may be ± 30% RSD. *(See Appendix D.)* A second source check is analyzed after each initial curve, to verify that the standards are correct.

6.4.2 Daily, a Continuing Calibration Check (CCC) is performed after the BFB tune check which is the start of every 24 hour clock. The CCC sample consists of the mid-level calibration standard. For the "Standard" TO-14 list compounds (*See Appendix A*), the relative percent difference for 90 % of the check compounds must be ≤ 30% from the five point average for the calibration to still be valid. For the "Non-standard and Polar" TO-14 list compounds (*See Appendix A*), the relative percent difference for 80 % of the check compounds must be ≤ 40% from the five point average for the calibration to still be valid. If the CCC fails to meet the performance

criteria then maintenance should be performed and the test repeated. If the system still fails the calibration check, a new 5 point calibration curve is performed. The sample results are calculated using the relative response factors from the daily calibration check or from the average from the initial curve if that is required by the project.

6.4.3 A laboratory fortified method spike is prepared by spiking all target species into humidified zero grade air at a concentration near the mid-low or mid point of the calibration curve (ca. 25 or 50 ppbv). The percent recovery (%R) acceptance criteria is ± 70 - 130% for the "Standard" TO-14 list compounds (*See Appendix A*). The %R acceptance criteria is ± 60 - 140% for the "Non-standard and Polar" TO-14 compounds (*See Appendix A*). When requested, the method spike and method spike duplicate are analyzed at a 10% frequency. The method spike %Rs are reported with the analytical results when sample duplicate analyses are reported.

6.4.4 A laboratory blank is run after the CCC at the beginning of each day and at least once in every 24 hour shift. Laboratory blanks should be run after every high level sample to demonstrate that contamination does not exist in the chromatographic system. The acceptance criteria for reagent blanks is for contamination less than the laboratory detection limit except for common lab solvents such as methylene chloride which should be less than 5X the reporting limit.

6.4.5 A daily tune check with 4-Bromofluorobenzene (BFB) is achieved by injecting 2 µL (50 nG) of the BFB Check Sample in accordance with CLP tuning criteria. Analysis cannot proceed unless all criteria (*Appendix F*) of the tune check are met.

6.4.6 The method analysis sequence is as follows and repeats every 24 hours (every 12 hours when project specified):

Initial 24 hour period:	BFB Tune Check
	5 Point Calibration
	Laboratory Blank
	Samples
Subsequent 24 hour period:	BFB Tune Check
	CCC Check/Method Spike
	Laboratory Blank
	Samples

The "Subsequent 24 hour" sequence is followed each twenty four hour period (every 12 hours when specified by the project) that samples are analyzed, until the system is found to be out of calibration.

6.4.7 All Internal Standard areas of the Laboratory Blank and all samples must be within ±40% of the CCC's Internal Standard area. The Retention Time of the Internal standard must be within ±0.5 min. of the CCC's Internal Standard Retention Time. When samples are analyzed on the same 24 hour clock as the initial calibration curve, the mid-point standard will be used for evaluation of Internal Standards. If either of the above criteria are not met, the sample (or blank) must be analyzed again (unless an obvious matrix interference is documented). If the criteria is still not met (it must be met for the blank, before analyses may continue), then the data is reported from the first analysis and the matrix effect narrated in the laboratory narrative included with the data report. Upon request, the data from the matrix effect confirmation analysis is provided to the client.

6.4.8 All Surrogate Recoveries of the Laboratory Blank and all samples must be within 70% to 130%. If the recovery limits are not met, the sample (or blank) must be analyzed again (unless an obvious matrix interference is documented). If the limits are still not met (they must be met for the blank, for analyses to continue), then the data is reported from the first analysis and the out of limit surrogate flagged with a "Q" qualifier. The "Q" qualifier is defined in the data package. For CLP-like packages, the qualifier is defined in the laboratory narrative.

6.4.9 A duplicate sample analysis is performed on 10% of the samples. The Relative Percent Difference (RPD) between the two analyses must be ≤ 30% RPD for all compounds detected at greater than 5 times the LOQ. If this limit is exceeded, the sample is re-analyzed a second time. If the limit is exceeded again, the cause is investigated and the system brought back to working order. If no problem is found on the system, the data is reported and a note describing the non-conforming event is provided with the final report.

6.4.10 Method Detection Limit Studies (MDL) are analyzed as described in 40 CFR Pt. 136 App.B. The MDL determines the 99% confidence level for seven replicates of a low level standard. The MDL is defined as 3.14 times the standard deviation of the seven replicates. See *Appendix G* for the MDL study results

7.0 DELIVERABLES

7.1 Standard (**Non-CLP-like**) **Data Reporting Package**

An example of a commercial data package reporting format appears in *Appendix J.* The header contains information containing to date of sampling, date of analysis, dilution factor and unique laboratory identifiers for both the sample and the analysis files. The table of target analytes

follows with information provided for adjusted detection limit and amount detected. Surrogate recovery information appears generally at the bottom of the table along with QC acceptance windows.

A computer generated diskette may be specified by the project and is available in a variety of format styles (DBASE III, Lotus, ASCII or customized). It is the responsibility of the Systems Manager to oversee the generation of the diskettes and to review their content prior to submission.

7.2 LEVEL IV - EPA CLP-like Reporting Package

A Level IV data package contains all of the elements of a full CLP style deliverable. See *Appendix K* for an example. The deliverable includes:

Cover Sheet - Sample ID's and Dates Received
Laboratory Narrative
Volatile Organic Analysis Sheets
Tentatively Identified Compound Sheets
Method Blank Summary Sheets
Internal Standard Retention Time and Area Count Sheet
Surrogate Percent Recovery Sheet
Multilevel Calibration Summary Sheet
BFB Tune Sheet
Copies of COC, Airbills and Sample Tags
All associated instrument raw data and laboratory notebook run logs

LIST OF APPENDICES

A. COMPOUNDS AND REPORTING LIMITS
B. NEAT MATERIALS MIX - DENSITY/SPIKE AMOUNTS
C. BFB CHECK MIX
D. INITIAL CALIBRATION DATA
E. QUANTITATION IONS
F. BFB TUNE CRITERIA
G. METHOD DETECTION LIMIT STUDY
H. Scott Specialty Gas Blend CERTIFICATES OF ANALYSIS
J. Non-CLP-like REPORTING FORMAT
K. LEVEL IV - CLP-like REPORTING FORMAT

Appendix A

COMPOUNDS AND REPORTING LIMITS

STANDARD LIST

Parameter	Det. Limit (ppbv) Ion Trap Full Scan	Det. Limit (ppbv) Quadrupole Full Scan
Freon 12	0.10	0.50
Chloromethane	0.10	0.50
Freon 114	0.10	0.50
Vinyl Chloride	0.10	0.50
Bromomethane	0.10	0.50
Chloroethane	0.10	0.50
Freon 11	0.10	0.50
1,1-Dichloroethene	0.10	0.50
Dichloromethane (Methylene Chloride)	0.10	0.50
Trichlorotrifluoroethane (Freon 113)	0.10	0.50
1,1-Dichloroethane	0.10	0.50
cis-1,2-Dichloroethene	0.10	0.50
Chloroform	0.10	0.50
1,2-Dichloroethane	0.10	0.50
Methyl Chloroform (1,1,1-Trichloroethane)	0.10	0.50
Benzene	0.10	0.50
Carbon Tetrachloride	0.10	0.50
1,2-Dichloropropane	0.10	0.50
Trichloroethene	0.10	0.50
cis-1,3-Dichloropropene	0.10	0.50
trans-1,3-Dichloropropene	0.10	0.50
1,1,2-Trichloroethane	0.10	0.50
Toluene	0.10	0.50
1,2-Dibromoethane (EDB)	0.10	0.50
Tetrachloroethene	0.10	0.50
Chlorobenzene	0.10	0.50
Ethylbenzene	0.10	0.50
m,p-Xylene	0.10	0.50
o-Xylene	0.10	0.50
Styrene	0.10	0.50
1,1,2,2-Tetrachloroethane	0.10	0.50
1,3,5-Trimethylbenzene	0.10	0.50
1,2,4-Trimethylbenzene	0.10	0.50
1,2-Dichlorobenzene	0.10	0.50
Chlorotoluene (Benzyl Chloride)	0.10	0.50
1,4-Dichlorobenzene	0.10	0.50
1,3-Dichlorobenzene	0.10	0.50
1,2,4-Trichlorobenzene	0.10	0.50
Hexachlorobutadiene	0.10	0.50

Appendix A - cont.

COMPOUNDS AND REPORTING LIMITS
NON-STANDARD AND POLAR LIST

Parameter	Det. Limit (ppbv) Ion Trap Full Scan	Det. Limit (ppbv) Quadrupole Full Scan
Propylene	0.50	2.0
1,3-Butadiene	0.50	2.0
Acetone	0.50	2.0
Carbon Disulfide	0.50	2.0
Isopropanol	0.50	2.0
trans-1,2-Dichloroethene	0.50	2.0
Vinyl Acetate	0.50	2.0
Chloroprene	0.50	2.0
2-Butanone (Methyl Ethyl Ketone)	0.50	2.0
Hexane	0.50	2.0
Tetrahydrofuran	0.50	2.0
Cyclohexane	0.50	2.0
1,4-Dioxane	0.50	2.0
Bromodichloromethane	0.50	2.0
4-Methyl-2-Pentanone (MIBK)	0.50	2.0
2-Hexanone	0.50	2.0
Dibromochloromethane	0.50	2.0
Bromoform	0.50	2.0
4-Ethyltoluene	0.50	2.0
Ethanol	0.50	2.0
Methy t-Butyl Ether (MTBE)	0.50	2.0
Heptane	0.50	2.0

Appendix B

ATLIST.XLS 6/21/95 1:09 PM

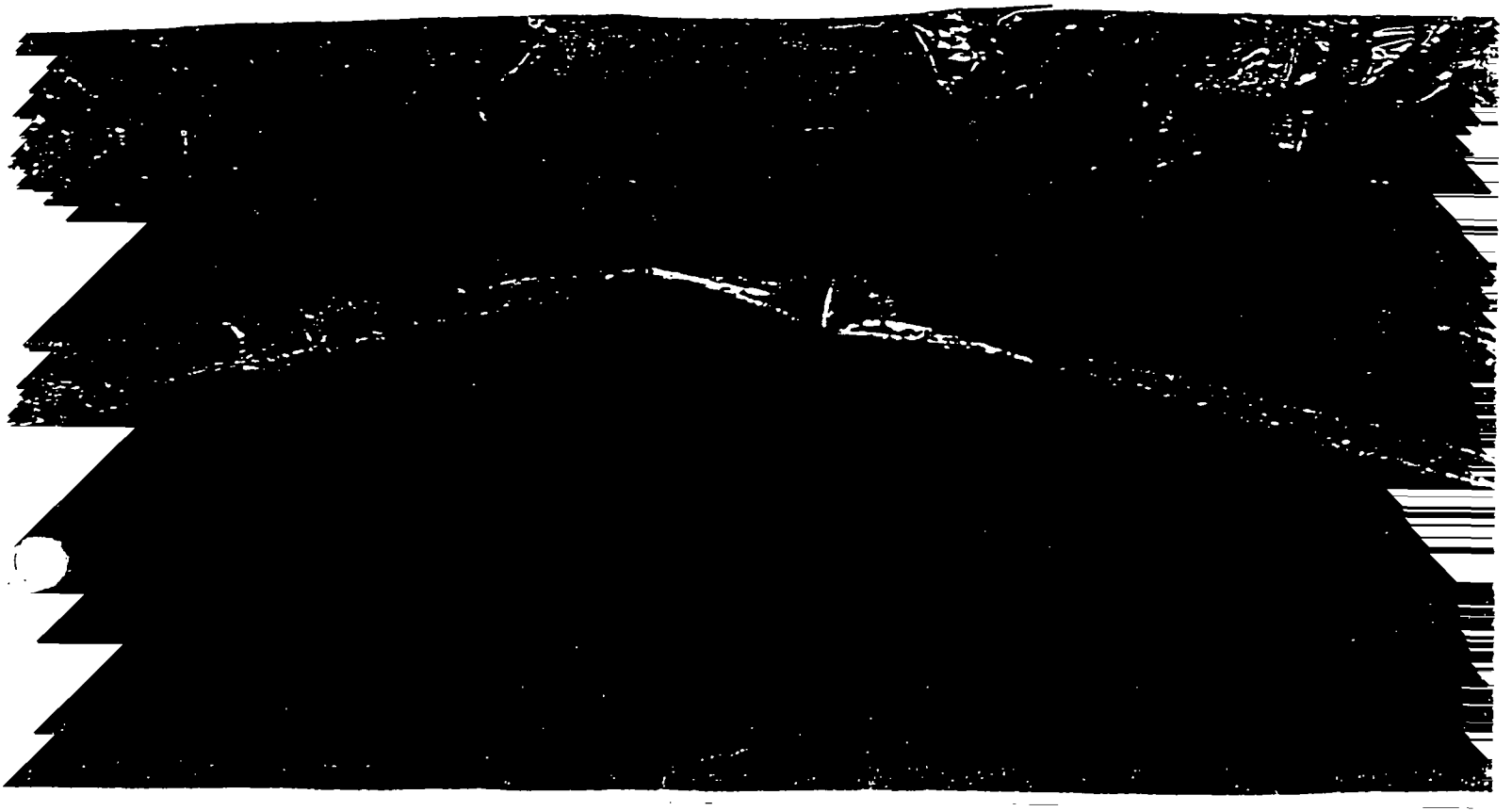
				8 Liter Gas Standards				
6/21/95								
Compound	**Supplier**	**Lot#**	**urit**	**CAS #**	**density**	**FW**	**uL**	**PPM**
1,3-Butadiene	Aldrich	14030MZ	99%	106-99-0	GAS	N/A	0.8ml	100
Propylene	Aldrich	10619DY	99+%	115-07-1	GAS	N/A	0.8ml	100
Cyclohexane	Aldrich	01314LV	99+%	110-82-7	0.779	84.16	3.6	100
n-Octane	Aldrich	00801MX	99+%	111-65-9	0.703	114.23	5.4	100
Bromoform	Aldrich	10226MX	99+%	75-25-2	2.894	252.75	2.9	100
Acetone	Sig-Aldrich	06247BF	99+%	67-64-1	0.791	58.08	2.5	102
Chloroprene	hem Servic	54-72A	50%	126-99-8	0.958	88.00	3.2	105 6.4
Bromodichloromethane	Aldrich	08830EY	99+%	75-27-4	1.980	163.83	2.8	102
Carbon Disulfide	EM	32324	99+%	75-15-0	1.266	76.14	2.0	100
Chlorodibromomethane	Aldrich	00925HP	98+%	124-48-1	2.451	208.29	2.9	103
Vinyl Acetate	Aldrich	05530AY	99+%	108-05-4	0.934	86.09	3.1	101
2-Propanol	B&J	AS575	99+%	67-63-0	0.785	60.1	2.6	102
Tetrahydrofuran	Aldrich	07815CX	99+%	109-99-9	0.886	72.11	2.7	100
t-1,2-Dichloroethene	Aldrich	10406EY	98+%	150-60-5	1.257	96.94	2.6	101
MEK	Aldrich	09119JW	99+%	78-93-3	0.805	72.11	3.0	101
MIBK	Aldrich	01427LW	99+%	108-10-1	0.812	86.13	3.6	102
2-Hexanone	Aldrich	01418BM	99+%	591-78-6	0.812	100.16	4.1	100
4-Ethyl Toluene	Aldrich	00103DM	98+%	622-96-8	0.861	120.2	4.6	99
1,4-Dioxane	Aldrich	02502CX	99+%	123-91-1	1.034	88.11	2.9	102
MTBE	Aldrich	02409EW	99+%	1634-04-4	0.758	88.15	3.9	101
Ethanol	Aldrich	01218JY	95%	64-17-5	0.785	46.07	2.0	102
Heptane	Aldrich	04410HV	99+%	142-82-5	0.684	100.21	4.9	101
2-Chloroethylvinylether	Aldrich	12011EW	99%	110-75-8	1.048	106.55	3.5	104
Hexane	Aldrich	01517CZ	99%	110-54-3	0.659	86.18	4.5	103
Plus 20.0ul of H2O								

Procedure: Measures 8L nitrogen into a Tedlar bag and spike in amounts of analytes listed in the table. Chloroprene is 50% in xylene, so spike twice the amount listed for chloroprene.

Appendix B - cont.

BENZYLCL.XLS

5/6/95	8 Liter Gas Standards							
Compound	LOT#	SUPPLIE	PURITY	CAS #	density	FW	uL	PPM
zyl Chloride	12127cx	ALDRICH	99%	100-44-7	1.100	126.59	3.9	102
rene	03701DZ	ALDRICH	99%	100-42-5	0.909	104	3.9	102



STD. I.D 207-21

Date: 10/6/95

Analyst: [signature]

Appendix C

ULTRA SCIENTIFIC 250 Smith St., North Kingstown, RI 02852 401-294-9400

PURGEABLE GC/MS CALIBRATION STANDARD

STS-110 1 mL

2000 ug/mL IN METHANOL

A2LA CERTIFIED, CERTIFICATION # US8195

Lot No. G-0862 Exp. Date 7/96

LAB USE ONLY

Each ampoule contains the following component at 2000 µg/mL in methanol.

4-bromofluorobenzene (BFB)

ULTRA Scientific

250 Smith Street
North Kingstown, RI 02852

STS-110-1

4-BROMOFLUOROBENZENE SOLUTION

A2LA CERTIFIED

1 x 1 mL

For Research Use Only

401-294-9400

Material Safety Data Sheet (MSDS) Available

625 ul of BFB was spiked into MeOH. The final volume = 50 ml

final concentration =

(x ml)(2000 ug/ml) = (50 ml)(25 ug/ml)

x = 0.625 ml

= 625 ul

MeOH lot # = 34333

omnisolv

Continued on Page

Read and Understood By

[signature] 10/6/95 | [signature] 10-6-95

Signed | Date | Signed | Date

5ppbv low-point used for 1,4-Dioxane and Ethanol
2ppbv low-point for Bromoform taken from file # 5102403
4-Point used on Vinyl Acetate

Air Toxics Limited

INITIAL CALIBRATION DATA

Start Cal Date : 21-SEP-95 19:13
End Cal Date : 24-OCT-1995 18:53
Quant Method : ISTD
Origin : Force
Target Version : 3.10
Integrator : HP Genie
Method file : /chem/msd5.i/5-24oct95.b/TO14-1024AT.m
Cal Date : 25-Oct-1995 00:22 msd5
Curve Type : Average

Calibration File Names:
Level 1: /chem/msd5.i/5-24oct95.b/5102410.d
Level 2: /chem/msd5.i/5-24oct95.b/5102405.d
Level 3: /chem/msd5.i/5-24oct95.b/5102406.d
Level 4: /chem/msd5.i/5-24oct95.b/5102407.d
Level 5: /chem/msd5.i/5-24oct95.b/5102408.d

	Compound	2 Level 1	25 Level 2	50 Level 3	100 Level 4	200 Level 5	RRF	% RSD	
1	FC-72(1)	*****	*****	*****	*****	*****	*****	*****	<-
	(2)	0.60686	315	*****	*****	*****	158	140.877	<-
2	Chlorodifluoromethane/FR22	*****	*****	*****	*****	*****	*****	*****	<-
3	Propylene	0.79036	0.71098	0.64174	0.68151	0.63453	0.69182	9.135	
4	DICHLORODIFLUOROMETHANE/FR 12	3.80352	3.72555	3.52816	3.46377	3.16302	3.53680	7.095	
5	FREON 114	3.96616	4.01442	3.85129	3.83155	3.37012	3.80671	6.720	
7	1-Butene	1.45018	*****	*****	*****	*****	1.45018	0.000	
6	CHLOROMETHANE	0.82597	0.90609	0.99715	0.82716	0.73831	0.85894	11.344	
10	Methanol	*****	*****	*****	*****	*****	*****	*****	<-
8	VINYL CHLORIDE	1.00511	1.12570	1.06170	1.08248	0.93795	1.04259	6.986	
9	1,3-Butadiene	0.41160	0.63062	0.58714	0.67918	0.62925	0.58756	17.636	
11	BROMOMETHANE	1.14523	1.14663	1.06522	1.08121	0.93912	1.07548	7.871	
13	Ether	*****	*****	*****	*****	*****	*****	*****	
14	Vinyl Bromide	*****	*****	*****	*****	*****	*****	*****	<-
15	Pentane	*****	*****	*****	*****	*****	*****	*****	<-
12	CHLOROETHANE	1.01698	0.81456	0.76989	0.73729	0.62384	0.79251	18.163	
17	Bromoethane	*****	*****	*****	*****	*****	*****	*****	<-
16	TRICHLOROFLUOROMETHANE/ FR 11	3.63765	4.01125	3.81280	3.64974	3.12506	3.64730	9.017	
18	Cyclopentane	*****	*****	*****	*****	*****	*****	*****	<-
20	Freon 123	*****	0.94316	0.87354	0.80711	*****	0.87460	7.779	<-
21	Acrolein	*****	*****	*****	*****	*****	*****	*****	<-
19	Ethanol	0.29829	0.19818	0.19914	0.26897	0.24005	0.24090	18.152	
24	Methyl Iodide	*****	*****	*****	*****	*****	*****	*****	<-
22	FREON 113	3.31123	4.21426	4.01924	3.88068	3.33858	3.85280	8.463	
23	1,1-DICHLOROETHENE	1.57487	1.65953	1.61022	1.55083	1.32184	1.54346	8.453	
25	Acetone	1.44800	1.20411	1.05375	1.34308	1.27465	1.26472	11.729	
28	Allyl Chloride	1.52744	2.01662	1.85281	1.85622	2.11479	1.87357	11.911	

Air Toxics Limited

INITIAL CALIBRATION DATA

Start Cal Date : 21-SEP-95 19:13
End Cal Date : 24-OCT-1995 18:53
Quant Method : ISTD
Origin : Force
Target Version : 3.10
Integrator : HP Genie
Method file : /chem/msd5.i/5-24oct95.b/TO14-1024AT.m
Cal Date : 25-Oct-1995 00:22 msd5
Curve Type : Average

Compound	2 Level 1	25 Level 2	50 Level 3	100 Level 4	200 Level 5	RRF	% RSD	
27 Carbon Disulfide	2.48394	2.94441	2.62929	3.24564	2.95942	2.85254	10.518	
26 2-Propanol	2.04659	1.29449	1.34346	1.69233	1.52368	1.58011	19.273	
29 Acetonitrile	*****	*****	*****	*****	*****	*****	*****	<-
30 METHYLENE CHLORIDE	1.55838	1.32322	1.23197	1.20743	1.07666	1.27953	13.996	
33 Acrylonitrile	*****	*****	*****	*****	*****	*****	*****	<-
31 MTBE	2.81430	3.24368	3.01800	3.53187	3.26721	3.17501	8.558	
32 trans-1,2-Dichloroethene	0.88348	1.26527	1.10760	1.35827	1.26495	1.17591	15.873	
34 1-Propanol	*****	*****	*****	*****	*****	*****	*****	
35 Hexane	2.30650	2.53309	2.21198	2.66869	2.43019	2.43009	7.430	
36 Allyl Alcohol	*****	*****	*****	*****	*****	*****	*****	<-
37 1,1-DICHLOROETHANE	2.76142	2.82204	2.72101	2.69718	2.44545	2.68942	5.367	
38 Vinyl Acetate	*****	1.97753	2.12759	3.03944	3.15616	2.57500	23.627	
39 Chloroprene	0.67629	1.04111	0.93334	1.14029	1.05170	0.96855	18.493	
40 1,2-Epoxybutane	*****	*****	*****	*****	*****	*****	*****	<-
41 Ethylesteraceticacid	*****	*****	*****	*****	*****	*****	*****	<-
42 cis-1,2-DICHLOROETHENE	1.47035	1.64723	1.55662	1.55874	1.42542	1.53167	5.631	
43 2-Butanone	0.27625	0.45268	0.43844	0.54348	0.54920	0.45201	24.458	
44 Tetrahydrofuran	1.03455	1.25743	1.13343	1.44985	1.46302	1.26766	14.958	
46 CHLOROFORM	2.69005	2.96643	2.86085	2.80261	2.58033	2.78005	5.388	
47 Isopropyl Acetate	*****	*****	*****	*****	*****	*****	*****	
50 CARBON TETRACHLORIDE	2.01345	2.67825	2.64841	2.59917	2.39996	2.46785	11.193	
48 Cyclohexane	1.60354	2.16725	1.91407	2.30474	2.12397	2.02271	13.498	
49 1,1,1-TRICHLOROETHANE	2.56240	2.97863	2.81293	2.74446	2.49720	2.71912	7.136	
51 Isobutanol	*****	*****	*****	*****	*****	*****	*****	<-
53 Isooctane	*****	*****	*****	*****	*****	*****	*****	<-
56 Methyl Cellosolve	*****	*****	*****	*****	*****	*****	*****	
55 1,2-DICHLOROETHANE	0.23884	0.29031	0.27087	0.27956	0.26087	0.26809	7.321	
54 BENZENE	0.95591	1.01238	0.94182	0.97770	0.91873	0.96131	3.714	
58 1-Butanol	*****	*****	*****	*****	*****	*****	*****	
59 Methylcyclohexane	*****	*****	*****	*****	*****	*****	*****	<-
57 Heptane	0.72006	0.78911	0.66322	0.86481	0.79270	0.76598	10.046	
61 Bicycloheptadiene	*****	*****	*****	*****	*****	*****	*****	<-
62 Propylesteraceticacid	*****	*****	*****	*****	*****	*****	*****	
63 Ethyl acrylate	*****	*****	*****	*****	*****	*****	*****	<-

Air Toxics Limited

INITIAL CALIBRATION DATA

Start Cal Date : 21-SEP-95 19:13
End Cal Date : 24-OCT-1995 18:53
Quant Method : ISTD
Origin : Force
Target Version : 3.10
Integrator : HP Genie
Method file : /chem/msd5.i/5-24oct95.b/TO14-1024AT.m
Cal Date : 25-Oct-1995 00:22 msd5
Curve Type : Average

Compound	2 Level 1	25 Level 2	50 Level 3	100 Level 4	200 Level 5	RRF	% RSD	
64 TRICHLOROETHENE	0.55792	0.56161	0.53355	0.53022	0.49216	0.53509	5.197	
65 Methyl Methacrylate	-----	-----	-----	-----	-----	-----	-----	<-
67 Ethyl Cellosolve	-----	-----	-----	-----	-----	-----	-----	
68 Dibromomethane	0.56713	-----	0.57334	0.45681	-----	0.53243	12.313	<-
66 1,2-DICHLOROPROPANE	0.44033	0.49071	0.47137	0.45938	0.43004	0.45836	5.281	
69 1,4-Dioxane	0.08719	0.13879	0.13636	0.19181	0.19281	0.14940	29.625	
70 Bromodichloromethane	0.34134	0.56837	0.49492	0.66631	0.62960	0.54011	23.835	
71 DMDS	-----	-----	-----	-----	-----	-----	-----	<-
72 c-1,3-DICHLOROPROPENE	0.35140	0.44222	0.44643	0.46173	0.44691	0.42974	10.334	
75 2,4-Pentanedione	-----	-----	-----	-----	-----	-----	-----	
73 4-Methyl-2-pentanone	0.94770	0.56466	0.56466	0.80615	0.76334	0.72930	22.632	
78 Iso-Butyl acetate	-----	-----	-----	1.30320	-----	1.30320	0.000	<-
77 TOLUENE	0.65174	0.67661	0.63313	0.64738	0.62407	0.64659	3.109	
76 Octane	0.38449	0.38534	0.31705	0.42025	0.39397	0.38022	10.038	
79 t-1,3-DICHLOROPROPENE	0.19989	0.19806	0.23268	0.23429	0.24491	0.22197	9.693	
82 1,3-DICHLOROPROPANE	-----	-----	-----	-----	-----	-----	-----	<-
80 1,1,2-TRICHLOROETHANE	0.61283	0.66623	0.65867	0.62539	0.61370	0.63536	3.992	
84 Butylesteraceticacid	-----	-----	-----	-----	-----	-----	-----	<-
81 TETRACHLOROETHENE	0.90351	0.97568	0.93412	0.85888	0.83729	0.90190	6.200	
83 2-Hexanone	0.60852	0.41488	0.37208	0.45556	0.44048	0.45830	19.580	
85 Dibromochloromethane	0.65791	0.88292	0.78805	1.02291	1.00032	0.87042	17.445	
86 1,2-DIBROMOETHANE	0.75346	0.94651	1.00790	0.99488	0.99581	0.93971	11.359	
87 Nonane	-----	-----	-----	-----	-----	-----	-----	<-
89 CHLOROBENZENE	1.11333	1.15024	1.15089	1.08810	1.10066	1.12064	2.564	
90 ETHYL BENZENE	0.65279	0.77166	0.74471	0.73619	0.73723	0.72852	6.136	
91 m,p-XYLENE	0.84338	0.90266	0.86576	0.87413	0.86316	0.86982	2.477	
92 Cellosolve Acetate	-----	-----	-----	-----	-----	-----	-----	
94 Isopropylbenzene	-----	-----	-----	-----	-----	-----	-----	<-
96 Butyl Cellosolve	-----	-----	-----	-----	-----	-----	-----	
93 o-XYLENE	0.55150	0.62228	0.58878	0.56622	0.57991	0.58174	4.590	
95 STYRENE	0.93877	0.64025	0.70006	0.96224	1.03105	0.85447	20.240	
97 Cyclohexanone	-----	-----	-----	-----	-----	-----	-----	
99 Cumene	-----	-----	-----	-----	-----	-----	-----	<-
98 Bromoform	0.46858	0.42365	0.37517	0.52997	0.52036	0.46350	14.092	

Air Toxics Limited

INITIAL CALIBRATION DATA

Start Cal Date : 21-SEP-95 19:13
End Cal Date : 24-OCT-1995 18:53
Quant Method : ISTD
Origin : Force
Target Version : 3.10
Integrator : HP Genie
Method file : /chem/msd5.i/5-24oct95.b/TO14-1024AT.m
Cal Date : 25-Oct-1995 00:22 msd5
Curve Type : Average

	Compound	2 Level 1	25 Level 2	50 Level 3	100 Level 4	200 Level 5	RRF	% RSD	
	101 Decane	*****	*****	*****	*****	*****	*****	*****	<-
	102 n-Propylbenzene	*****	*****	*****	*****	*****	*****	*****	<-
	103 1,1,2,2-TETRACHLOROETHANE	1.06504	1.24208	1.22886	1.16975	1.24568	1.19028	6.418	
	104 4-Ethyltoluene	0.35367	0.65063	0.62681	0.57319	0.59697	0.56025	21.267	
	16 3-Octanone	*****	*****	*****	*****	*****	*****	*****	
	105 1,3,5-TRIMETHYLBENZENE	1.98399	1.51744	1.24827	1.85270	1.75010	1.67050	17.440	
	107 alpha-Methyl Styrene	*****	*****	*****	*****	*****	*****	*****	<-
	109 1,2,3-Trimethylbenzene	*****	*****	*****	*****	*****	*****	*****	<-
	110 sec-Butyl-benzene	*****	*****	*****	*****	*****	*****	*****	<-
	108 1,2,4-TRIMETHYLBENZENE	1.26878	1.03751	0.97889	0.87810	0.96852	1.02636	14.326	
	111 P-Cymene	*****	*****	*****	*****	*****	*****	*****	<-
	112 Dicyclopentadiene	*****	*****	*****	*****	*****	*****	*****	<-
	113 1,3-DICHLOROBENZENE	0.83586	1.01072	1.01993	0.94885	1.03969	0.97101	8.530	
	114 1,4-DICHLOROBENZENE	1.23519	1.14855	1.06541	0.97753	1.08303	1.10194	8.739	
	115 BENZYL CHLORIDE	0.74571	0.69183	0.75679	1.05039	1.21765	0.89247	25.727	
	116 1,2-DICHLOROBENZENE	1.11058	0.89373	0.91154	0.82589	0.89912	0.92817	11.559	
	117 1,2-DB-3CPA	*****	*****	*****	*****	*****	*****	*****	<-
	118 1,3,5-Trichlorobenzene	*****	*****	*****	*****	*****	*****	*****	<-
	119 Isophorone	*****	*****	*****	*****	*****	*****	*****	<-
	120 1,2,4-TRICHLOROBENZENE	0.27276	0.23550	0.34596	0.33063	0.38839	0.31465	19.261	
	121 HEXACHLOROBUTADIENE(1)	0.75099	0.64309	0.56426	0.44531	0.50120	0.58097	20.693	
	(2)	0.48971	0.41070	0.36248	0.28646	0.31566	0.37300	21.586	
S	52 Octafluorotoluene	2.71702	2.61782	2.65043	2.51332	2.52310	2.60434	3.319	
S	74 Toluene-d8	0.85079	0.90260	0.88075	0.91933	0.90673	0.89204	3.019	
S	100 BFB	0.91386	1.00876	0.98928	1.01823	1.00898	0.98782	4.320	

Air Toxics Limited

COMPOUND LISTING

ethod file : /tp/target/itd7.i/7sat0807.m
uant Method : ISTD Target Version : 3.10
ast Update : 08-Sep-1995 11:11 Number of Cpnds : 78
ata Type : MS DATA

lobal Integrator : HP RTE

hromat Events	Values
nitial:Thresh Units	1.000000
nitial:Area Thresh	5.000000
nitial:Max Peaks	100.000000
nitial:Bunching	1.000000
nitial:Smoothing	0.000000
nitial:Start Thresh	0.200000
nitial:Stop Thresh	0.000000
nitial:Baseline Reset	5.000000
nitial:Set Valley	100.000000

The first mass listed for each compound is used for quantitation.

	Compound	RT	RT Window	RF	Mass	Int. Std.
1	Ethanol	12.291	11.291-13.291	0.000	45.00	#1
		12.291	11.291-13.291	0.000	46.00	
		12.291	11.291-13.291	0.000	43.00	
2	Propylene	9.346	7.346-11.346	0.000	39.00	
		9.346	7.346-11.346	0.000	41.00	
3	Chlorodifluoromethane(FR22	6.760	4.760-8.760	0.000	51.00	
		6.760	4.760-8.760	0.000	67.00	
4	Acetone	12.772	11.772-13.772	0.001	43.00	
		12.772	11.772-13.772	0.000	58.00	
5	Carbon Disulfide	14.305	13.305-15.305	0.001	76.00	
6	DICHLORODIFLUOROMETHANE/FR	6.694	5.694-7.694	0.000	85.00	
		6.694	5.694-7.694	0.000	87.00	
7	2-Propanol	13.465	12.465-14.465	0.000	45.00	
		13.465	12.465-14.465	0.000	43.00	
		13.465	12.465-14.465	0.000	59.00	
8	CHLOROMETHANE	7.627	6.627-8.627	5.3e-05	50.00	
		7.627	6.627-8.627	0.000	52.00	
9	MTBE	15.931	13.931-17.931	0.000	73.00	
10	trans-1,2-Dichloroethene	15.505	14.505-16.505	0.000	96.00	
		15.505	14.505-16.505	0.000	61.00	
		15.505	14.505-16.505	0.000	98.00	
11	FREON 114	8.612	7.612-9.612	0.001	135.00	
		8.612	7.612-9.612	0.000	137.00	

Int Std #1 - 1,4-Difluorobenzene
Int. Std. #2 - Chlorobenzene-d5

Air Toxics Limited

COMPOUND LISTING

Method file : /tp/target/itd7.i/7sat0807.m

Compound	RT	RT Window	RF	Mass
12 VINYL CHLORIDE	8.780	7.780-9.780	0.000	62.00
	8.780	7.780-9.780	0.000	64.00
13 1,3-Butadiene	9.517	8.517-10.517	0.000	39.00
	9.517	8.517-10.517	0.000	54.00
14 Methanol	9.880	7.880-11.880	0.000	31.00
	9.880	7.880-11.880	0.000	32.00
15 Vinyl Acetate	16.079	15.079-17.079	0.000	43.00
	16.079	15.079-17.079	0.000	86.00
16 Chloroprene	16.479	15.479-17.479	0.000	53.00
	16.479	15.479-17.479	0.000	88.00
	16.479	15.479-17.479	0.000	50.00
17 BROMOMETHANE	10.530	9.530-11.530	8.0e-05	94.00
	10.530	9.530-11.530	0.000	96.00
18 CHLOROETHANE	11.198	10.198-12.198	2.7e-05	49.00
	11.198	10.198-12.198	0.000	64.00
	11.198	10.198-12.198	0.000	66.00
19 Acetonitrile	13.940	11.940-15.940	0.000	41.00
	13.940	11.940-15.940	0.000	40.00
	13.940	11.940-15.940	0.000	38.00
20 Acrolein	10.690	8.690-12.690	0.000	55.00
	10.690	8.690-12.690	0.000	56.00
	10.690	8.690-12.690	0.000	53.00
21 2-Butanone(MEK)	16.332	15.332-17.332	0.001	43.00
	16.332	15.332-17.332	0.000	72.00
	16.332	15.332-17.332	0.000	57.00
22 Tetrahydrofuran	17.666	16.666-18.666	8.6e-05	42.00
	17.666	16.666-18.666	0.000	71.00
	17.666	16.666-18.666	0.000	72.00
23 TRICHLOROFLUOROMETHANE/ FR	12.973	11.973-13.973	0.001	101.00
	12.973	11.973-13.973	0.000	103.00
24 Acrylonitrile	11.806	9.806-13.806	0.000	52.00
	11.806	9.806-13.806	0.000	54.00
25 Pentane	11.843	9.843-13.843	0.000	41.00
	11.843	9.843-13.843	0.000	57.00
	11.843	9.843-13.843	0.000	71.00
26 1,1-DICHLOROETHENE	14.040	13.040-15.040	0.000	96.00
	14.040	13.040-15.040	0.000	61.00
	14.040	13.040-15.040	0.000	98.00
27 3-Chloropropene	12.356	10.356-14.356	0.000	39.00
	12.356	10.356-14.356	0.000	41.00
	12.356	10.356-14.356	0.000	76.00

Air Toxics Limited

COMPOUND LISTING

Method file : /tp/target/itd7.i/7sat0807.m

	Compound	RT	RT Window	RF	Mass
28	Hexane	14.268	12.268-16.268	0.000	56.00
		14.268	12.268-16.268	0.000	84.00
		14.268	12.268-16.268	0.000	41.00
29	METHYLENE CHLORIDE	14.333	13.333-15.333	0.000	49.00
		14.333	13.333-15.333	0.000	84.00
		14.333	13.333-15.333	0.000	51.00
30	FREON 113	14.759	13.759-15.759	0.000	151.00
		14.759	13.759-15.759	0.000	153.00
		14.759	13.759-15.759	0.000	101.00
31	Heptane	20.345	19.345-21.345	0.000	41.00
		20.345	19.345-21.345	0.000	43.00
		20.345	19.345-21.345	0.000	57.00
32	1,1-DICHLOROETHANE	15.919	14.919-16.919	3.1e-05	63.00
		15.919	14.919-16.919	0.000	65.00
33	cis-1,2-DICHLOROETHENE	16.990	15.990-17.990	4.9e-05	96.00
		16.990	15.990-17.990	0.000	61.00
		16.990	15.990-17.990	0.000	98.00
34	CHLOROFORM	17.300	16.300-18.300	0.000	83.00
		17.300	16.300-18.300	0.000	85.00
35	1,4-Dioxane	20.026	19.026-21.026	8.9e-05	88.00
		20.026	19.026-21.026	0.000	58.00
		20.026	19.026-21.026	0.000	57.00
36	Bromodichloromethane	19.932	18.932-20.932	0.000	83.00
		19.932	18.932-20.932	0.000	85.00
$ 37	Octafluorotoluene (Surr.)	18.160	17.160-19.160	0.632	217.00
		18.160	17.160-19.160	0.000	186.00
38	1,2-DICHLOROETHANE	18.160	17.160-19.160	2.8e-05	62.00
		18.160	17.160-19.160	0.000	64.00
39	1,1,1-TRICHLOROETHANE	18.439	17.439-19.439	0.001	97.00
		18.439	17.439-19.439	0.000	99.00
40	BENZENE	18.946	17.946-19.946	0.001	78.00
		18.946	17.946-19.946	0.000	77.00
41	Cyclohexane	19.091	17.091-21.091	0.000	84.00
		19.091	17.091-21.091	0.000	56.00
		19.091	17.091-21.091	0.000	41.00
42	CARBON TETRACHLORIDE	19.106	18.106-20.106	0.001	117.00
		19.106	18.106-20.106	0.000	119.00
43	4-Methyl-2-pentanone	21.025	20.025-22.025	0.000	43.00
		21.025	20.025-22.025	0.000	58.00
		21.025	20.025-22.025	0.000	85.00

Surr. = 1

Air Toxics Limited

COMPOUND LISTING

Method file : /tp/target/itd7.i/7sat0807.m

	Compound	RT	RT Window	RF	Mass
	44 2-Hexanone	22.425	21.425-23.425	0.000	43.00
		22.425	21.425-23.425	0.000	58.00
		22.425	21.425-23.425	0.000	100.00
*	45 1,4-Difluorobenzene	19.373	18.373-20.373	1940883	114.00
		19.373	18.373-20.373	0.000	88.00
	46 Octane	23.306	22.306-24.306	0.000	41.00
		23.306	22.306-24.306	0.000	85.00
		23.306	22.306-24.306	0.000	43.00
	47 1,2-DICHLOROPROPANE	19.759	18.759-20.759	0.000	39.00
		19.759	18.759-20.759	0.000	63.00
		19.759	18.759-20.759	0.000	62.00
	48 Methyl Methacrylate	16.982	14.982-18.982	0.000	39.00
		16.982	14.982-18.982	0.000	69.00
		16.982	14.982-18.982	0.000	99.00
	49 TRICHLOROETHENE	20.100	19.100-21.100	0.000	130.00
		20.100	19.100-21.100	0.000	95.00
		20.100	19.100-21.100	0.000	97.00
	50 2-Chloroethylvinylether	20.640	18.640-22.640	6.1e-05	63.00
		20.640	18.640-22.640	0.000	65.00
		20.640	18.640-22.640	0.000	43.00
	51 c-1,3-DICHLOROPROPENE	21.092	20.092-22.092	0.000	75.00
		21.092	20.092-22.092	0.000	77.00
		21.092	20.092-22.092	0.000	39.00
	52 Dibromochloromethane	22.586	21.586-23.586	0.001	129.00
		22.586	21.586-23.586	0.000	208.00
	53 t-1,3-DICHLOROPROPENE	21.692	20.692-22.692	0.000	75.00
		21.692	20.692-22.692	0.000	77.00
	54 1,1,2-TRICHLOROETHANE	21.870	20.870-22.870	0.000	61.00
		21.870	20.870-22.870	0.000	97.00
		21.870	20.870-22.870	0.000	99.00
$	55 Toluene-d8 (Surr.)	22.059	21.059-23.059	1.265	98.00
		22.059	21.059-23.059	0.000	70.00
		22.059	21.059-23.059	0.000	100.00
	56 TOLUENE	22.266	21.266-23.266	0.004	91.00
		22.266	21.266-23.266	0.000	92.00
	57 1,2-DIBROMOETHANE	23.000	22.000-24.000	0.001	107.00
		23.000	22.000-24.000	0.000	109.00
	58 TETRACHLOROETHENE	23.586	22.586-24.586	0.001	166.00
		23.586	22.586-24.586	0.000	129.00
		23.586	22.586-24.586	0.000	131.00
	59 Chlorobenzene-d5	24.386	23.386-25.386	1472440	117.00
		24.386	23.386-25.386	0.000	82.00

Air Toxics Limited

COMPOUND LISTING

Method file : /tp/target/itd7.i/7sat0807.m

	Compound	RT	RT Window	RF	Mass
60	CHLOROBENZENE	24.440	23.440-25.440	0.001	112.00
		24.440	23.440-25.440	0.000	114.00
		24.440	23.440-25.440	0.000	77.00
61	Bromoform	25.146	24.146-26.146	0.000	173.00
		25.146	24.146-26.146	0.000	171.00
62	ETHYL BENZENE	24.933	23.933-25.933	0.002	91.00
		24.933	23.933-25.933	0.000	106.00
63	m,p-XYLENE	25.079	24.079-26.079	0.003	91.00
		25.079	24.079-26.079	0.000	106.00
64	STYRENE	25.666	24.666-26.666	3.0e-05	104.00
		25.666	24.666-26.666	0.000	78.00
65	1,1,2,2-TETRACHLOROETHANE	25.787	24.787-26.787	0.000	83.00
		25.787	24.787-26.787	0.000	85.00
66	o-XYLENE	25.813	24.813-26.813	0.002	91.00
		25.813	24.813-26.813	0.000	106.00
67	4-Ethyltoluene	27.520	26.520-28.520	0.001	105.00
		27.520	26.520-28.520	0.000	120.00
$ 68	BFB (Surr.)	26.400	24.400-28.400	0.689	95.00
		26.400	24.400-28.400	0.000	174.00
		26.400	24.400-28.400	0.000	176.00
69	alpha-Methyl Styrene	29.730	27.730-31.730	0.000	117.00
		29.730	27.730-31.730	0.000	103.00
		29.730	27.730-31.730	0.000	118.00
70	1,3,5-TRIMETHYLBENZENE	27.786	26.786-28.786	0.001	105.00
		27.786	26.786-28.786	0.000	120.00
71	1,2,4-TRIMETHYLBENZENE	28.519	27.519-29.519	0.000	105.00
		28.519	27.519-29.519	0.000	120.00
72	BENZYL CHLORIDE	25.813	24.813-26.813	0.000	91.00
		25.813	24.813-26.813	0.000	126.00
73	1,3-DICHLOROBENZENE	28.799	27.799-29.799	0.000	146.00
		28.799	27.799-29.799	0.000	148.00
		28.799	27.799-29.799	0.000	111.00
74	1,4-DICHLOROBENZENE	28.933	27.933-29.933	0.000	146.00
		28.933	27.933-29.933	0.000	148.00
		28.933	27.933-29.933	0.000	111.00
75	1,2-DICHLOROBENZENE	29.640	28.640-30.640	0.000	146.00
		29.640	28.640-30.640	0.000	148.00
		29.640	28.640-30.640	0.000	111.00
76	1,2,4-TRICHLOROBENZENE	33.920	32.920-34.920	0.000	180.00
		33.920	32.920-34.920	0.000	182.00

Air Toxics Limited

COMPOUND LISTING

Method file : /tp/target/itd7.i/7sat0807.m

Compound	RT	RT Window	RF	Mass
77 HEXACHLOROBUTADIENE	33.586	32.586-34.586	7.4e-05	225.00
	33.586	32.586-34.586	0.000	227.00
	33.586	32.586-34.586	0.000	260.00
147 Vinyl Bromide	13.430	11.430-15.430	0.000	106.00
	13.430	11.430-15.430	0.000	108.00

TABLE 4. 4-BROMOFLUOROBENZENE KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% but< 101% of mass 174
177	5 to 9% of mass 176

Appendix G

TO14 MDL study for AIST-1

MDL = 0.5 ppbv

Q Air Toxics Ltd.
METHOD DETECTION LIMIT SUMMARY REPORT

Method File: /chem/msd1.i/1-20Apr95.b/TO14-0320ATGn.m
Batch File: /chem/msd1.i/1-20Apr95.b
Inst ID: msd1.i

ID:	MDL01	MDL02	MDL03	MDL04	MDL05	MDL06	MDL07
FILENAME:	1042008	1042009	1042010	1042011	1042012	1042013	1042014
INJ.DATE:	20-APR-95	20-APR-95	20-APR-95	20-APR-95	20-APR-95	20-APR-95	20-APR-95
INJ.TIME:	13:13	13:57	14:38	15:17	16:05	16:50	17:51

Compound	MDL01	MDL02	MDL03	MDL04	MDL05	MDL06	MDL07	AVG CONC	STD DEV	MDL
1 Propylene	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
2 DICHLORODIFLUOROMETHAN	2.49	2.54	2.52	2.39	2.81	2.63	2.48	2.55	0.13	0.42
3 FREON 114	2.72	2.61	2.68	2.81	2.80	2.88	2.75	2.75	0.09	0.28
4 CHLOROMETHANE	2.53	2.56	2.87	2.68	2.51	2.52	2.67	2.62	0.13	0.41
5 VINYL CHLORIDE	2.33	2.32	2.51	2.26	2.50	2.26	2.23	2.34	0.12	0.36
6 1,3-Butadiene	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
7 BROMOMETHANE	1.92	2.06	2.05	1.96	2.12	2.12	2.08	2.05	0.08	0.25
8 CHLOROETHANE	2.40	2.43	2.19	2.16	2.37	2.28	2.25	2.30	0.10	0.33
9 TRICHLOROFLUOROMETHANE	2.52	2.57	2.51	2.45	2.78	2.72	2.59	2.59	0.12	0.37
10 Ethanol	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
11 FREON 113	2.36	2.44	2.32	2.53	2.64	2.34	2.33	2.42	0.12	0.38
12 1,1-DICHLOROETHENE	2.67	2.55	2.47	2.53	2.71	2.64	2.69	2.61	0.09	0.29
13 Acetone	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
14 Carbon Disulfide	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
15 2-Propanol	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
16 Allyl Chloride	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****

Reviewer 1 _____ Date: _____
Reviewer 2 _____ Date: _____

@ Air Toxics Ltd.
METHOD DETECTION LIMIT SUMMARY REPORT

Method File: /chem/msd1.i/1-20Apr95.b/TO14-0320ATGn.m
Batch File: /chem/msd1.i/1-20Apr95.b
Inst ID: msd1.i

	Compound	MDL01	MDL02	MDL03	MDL04	MDL05	MDL06	MDL07	AVG CONC	STD DEV	MDL
	17 METHYLENE CHLORIDE	2.30	2.28	2.62	2.63	2.44	2.34	2.29	2.41	0.16	0.49
	18 MIBE	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	19 trans-1,2-Dichloroethe	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	20 Acrylonitrile	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	21 Hexane	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	22 1,1-DICHLOROETHANE	2.34	2.31	2.37	2.30	2.33	2.35	2.29	2.33	0.03	0.09
	23 Vinyl Acetate	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	24 Chloroprene	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	25 cis-1,2-DICHLOROETHENE	2.00	2.09	2.17	2.02	2.08	2.20	2.15	2.11	0.06	0.20
	26 2-Butanone	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
*	27 Bromochloromethane	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00	0.00	0.00
	28 Tetrahydrofuran	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	29 CHLOROFORM	2.24	2.35	2.06	2.38	2.31	2.47	2.44	2.32	0.14	0.44
	30 Iso-Octane	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	31 Cyclohexane	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	32 1,1,1-TRICHLOROETHANE	2.37	2.38	2.30	2.39	2.46	2.37	2.44	2.39	0.05	0.17
	33 CARBON TETRACHLORIDE	2.34	2.46	2.33	2.74	2.58	2.34	2.52	2.47	0.15	0.48
$	34 Octafluorotoluene	48.80	45.51	44.60	43.33	46.43	46.17	48.93	46.26	2.05	6.45
	35 BENZENE	2.21	2.29	2.23	2.39	2.33	2.41	2.22	2.30	0.08	0.26
	36 1,2-DICHLOROETHANE	2.07	2.12	2.19	1.97	2.27	2.00	2.13	2.12	0.09	0.30
	37 Heptane	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
*	38 1,4-Difluorobenzene	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00	0.00	0.00

Reviewer 1 _____ Date: _____
Reviewer 2 _____ Date: _____

@ Air Toxics Ltd.
METHOD DETECTION LIMIT SUMMARY REPORT

Method File: /chem/msd1.i/1-20Apr95.b/TO14-0320ATGn.m
Batch File: /chem/msd1.i/1-20Apr95.b
Inst ID: msd1.i

	Compound	MDL01	MDL02	MDL03	MDL04	MDL05	MDL06	MDL07	AVG CONC	STD DEV	MDL
	39 1-Butanol	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	40 TRICHLOROETHENE	2.35	2.46	2.44	2.42	2.38	2.55	2.45	2.43	0.07	0.21
	41 1,2-DICHLOROPROPANE	2.29	2.35	2.41	2.33	2.41	2.47	2.41	2.38	0.06	0.19
	42 1,4-Dioxane	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	43 Bromodichloromethne	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	44 c-1,3-DICHLOROPROPENE	2.64	2.82	2.81	2.79	2.78	2.80	2.79	2.78	0.06	0.20
	45 4-Methyl-2-pentanone	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	46 Butyl Acetate	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
t	47 Toluene-d8	51.97	53.54	52.25	51.89	51.31	52.01	50.96	51.99	0.82	2.57
	48 TOLUENE	2.02	2.00	2.00	1.98	2.05	2.19	2.18	2.07	0.08	0.27
	49 Octane	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	50 t-1,3-DICHLOROPROPENE	2.00	1.89	1.97	1.96	2.19	1.93	2.09	2.00	0.10	0.32
	51 1,1,2-TRICHLOROETHANE	2.23	2.38	2.34	2.25	2.45	2.43	2.53	2.37	0.11	0.34
	52 TETRACHLOROETHENE	2.32	2.34	2.34	2.31	2.49	2.49	2.51	2.40	0.09	0.29
	53 2-Hexanone	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	54 Dibromochloromethane	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	55 1,2-DIBROMOETHANE	2.37	2.41	2.41	2.28	2.59	2.53	2.66	2.47	0.13	0.42
	56 Cumene	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
*	57 Chlorobenzene-d5	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00	0.00	0.00
	58 CHLOROBENZENE	2.24	2.35	2.17	2.19	2.35	2.35	2.46	2.30	0.10	0.33
	59 ETHYL BENZENE	2.41	2.38	2.17	2.26	2.20	2.23	2.34	2.28	0.09	0.29
	60 m,p-XYLENE	5.41	5.31	5.01	5.07	5.11	5.29	5.23	5.20	0.15	0.46

Reviewer 1 _____ Date: _____
Reviewer 2 _____ Date: _____

@ Air Toxics Ltd.
METHOD DETECTION LIMIT SUMMARY REPORT

Method File: /chem/msd1.i/1-20Apr95.b/TO14-0320ATGn.m
Batch File: /chem/msd1.i/1-20Apr95.b
Inst ID: msd1.i

	Compound	MDL01	MDL02	MDL03	MDL04	MDL05	MDL06	MDL07	AVG CONC	STD DEV	MDL
	61 o-XYLENE	2.03	2.04	1.88	1.95	2.02	2.11	2.16	2.03	0.09	0.29
	62 STYRENE	1.67	1.74	1.75	1.81	1.83	1.76	1.97	1.79	0.09	0.30
	63 Bromoform	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
$	64 BFB	48.16	48.89	48.39	49.67	49.22	47.71	48.00	48.58	0.71	2.23
	65 1,1,2,2-TETRACHLOROETH	2.52	2.65	2.52	2.62	2.87	2.81	2.81	2.68	0.14	0.44
	66 4-Ethyltoluene	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	67 1,3,5-TRIMETHYLBENZENE	2.32	2.47	2.37	2.35	2.55	2.57	2.36	2.43	0.10	0.32
	68 1,2,4-TRIMETHYLBENZENE	2.09	2.09	2.07	2.18	2.45	2.24	2.24	2.19	0.13	0.42
	69 1,3-DICHLOROBENZENE	2.00	2.05	2.01	1.98	2.33	2.18	2.24	2.11	0.14	0.43
	70 1,4-DICHLOROBENZENE	2.00	2.21	2.05	2.16	2.36	2.26	2.29	2.19	0.13	0.40
	71 Isooctyl Alcohol	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	72 BENZYL CHLORIDE	1.39	1.34	1.55	1.38	1.79	1.48	1.54	1.49	0.16	0.49
	73 1,2-DICHLOROBENZENE	2.04	2.15	1.99	2.04	2.42	2.26	2.29	2.17	0.16	0.49
	74 Isooctyl Acrylate	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	75 DBCP	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	76 1,2,4-TRICHLOROBENZENE	1.24	1.35	1.18	1.27	1.64	1.29	1.45	1.35	0.16	0.49
	77 HEXACHLOROBUTADIENE	2.64	2.54	2.50	2.62	2.80	2.74	2.84	2.67	0.13	0.40
	78 Dibromomethane	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	79 Methanol	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	80 Acrolein	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	81 Acetonitrile	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
	82 Ethyl Acetate	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****

Reviewer 1 _____ Date: _____
Reviewer 2 _____ Date: _____

Appendix H

FROM OTHER SIDE

ANALYSIS LEVEL

	HALOCARBON 11	4.[illegible]	PPM/M
	HALOCARBON 114	4.[illegible]	PPM/M
	HALOCARBON 12	4.[illegible]	PPM/M
	METHYLENE CHLORIDE	5.[illegible]	PPM/M
	1,1,2,2-TETRACHLOROETHANE	5.[illegible]	PPM/M
	1,1,2-TRICHLOROETHANE	5.[illegible]	PPM/M
	NITROGEN		BAL

Analysis Date [illegible] Project No 31-[illegible]

Accuracy +/-[illegible]% Analyst [illegible] Cylinder No. [illegible]

Scott Specialty Gases

CERTIFICATE OF ANALYSIS

AIR TOXICS LTD

PO No. [illegible]

CAS Reg Component No	Component	Certified Analysis	
74-83-9	BROMOMETHANE	5.[illegible]	PPM/M
74-87-3	CHLOROMETHANE	4.[illegible]	PPM/M
156-59-2	CIS 1,2-DICHLOROETHYLENE	5.27	PPM/M
95-50-1	1,2-DICHLOROBENZENE	5.25	PPM/M
541-73-1	1,3-DICHLOROBENZENE	5.[illegible]	PPM/M
106-46-7	1,4-DICHLOROBENZENE	5.[illegible]	PPM/M
75-34-3	1,1-DICHLOROETHANE	5.[illegible]	PPM/M
78-87-5	1,2-DICHLOROPROPANE	5.[illegible]	PPM/M
100-41-4	ETHYLBENZENE	5.37	PPM/M
75-00-3	ETHYL CHLORIDE	4.[illegible]	PPM/M

Scott Specialty Gases

CERTIFICATE OF ANALYSIS

LTD PO No. [illegible]

CAS Reg Component No.	Component	Certified Analysis	
	BENZENE	5.15	PPM/M
	CARBON TETRACHLORIDE	5.12	PPM/M
	CHLOROBENZENE	5.[illegible]	PPM/M
	CHLOROFORM	5.[illegible]	PPM/M
	CHLOROMETHYLBENZENE([illegible])	5.37	PPM/M
	CIS 1,3-DICHLOROPROPENE	7.[illegible]	PPM/M
	1,2-DIBROMOETHANE	5.[illegible]	PPM/M
	1,2-DICHLOROETHANE	5.[illegible]	PPM/M
	1,1-DICHLOROETHENE	5.25	PPM/M
	HALOCARBON 113	5.[illegible]	PPM/M

CONTINUED FROM OTHER SIDE

CERTIFIED ANALYSIS LEVEL

87-68-3	HEXACHLORO-1,3-BUTADIENE	5.04	PPM/M
100-42-5	STYRENE	5.[illegible]	PPM/M
127-18-4	TETRACHLOROETHYLENE	5.[illegible]	PPM/M
108-88-3	TOLUENE	5.[illegible]	PPM/M
10061-02-6	TRANS 1,3-DICHLOROPROPENE	5.[illegible]	PPM/M
71-55-6	1,1,1-TRICHLOROETHANE	5.[illegible]	PPM/M
79-01-6	TRICHLOROETHYLENE	5.[illegible]	PPM/M
120-82-1	1,2,4 TRICHLOROBENZENE	5.31	PPM/M
95-63-6	1,2,4-TRIMETHYLBENZENE	5.04	PPM/M
108-67-8	1,3,5-TRIMETHYLBENZENE	5.[illegible]	PPM/M

Scott Specialty Gases

CERTIFICATE OF ANALYSIS

FROM OTHER SIDE

ANALYSIS LEVEL

	VINYL CHLORIDE	4.[illegible]	PPM/M
	O-XYLENE	5.07	PPM/M
	M-XYLENE	5.[illegible]	PPM/M
	P-XYLENE	5.07	PPM/M
	NITROGEN		BAL

Analysis Date [illegible] Project No 31-[illegible]

Accuracy +/-[illegible]% Analyst [illegible] Cylinder No [illegible]

Item No. [illegible]

CONTINUED FROM OTHER SIDE

CERTIFIED ANALYSIS LEVEL

Item No [illegible]

Reorder/Service Contact [illegible] [illegible]

Template1

WORK ORDER #:

Work Order Summary

CLIENT:

BILL TO:

PHONE:
FAX:
DATE RECEIVED:
DATE COMPLETED:

INVOICE #
P.O. #
PROJECT #
AMOUNTS:

FRACTION #	NAME	TEST	RECEIPT VAC./PRES.	PRICE
01A		Template		
		Template		
		Template		
		Template		
		Template		
		Template		
		Template		
		Template		
		Template		
		Template		
		Template		
		Template		
		Template		
		Template		
		Template		
		Template		
		Template		
		Template		

CERTIFIED BY:_____ DATE:_____

Laboratory Director

Template-TO-14

AIR TOXICS LTD.

SAMPLE NAME:
ID#: -01A
EPA METHOD TO-14 GC/MS Full Scan

File Name:	Date of Collection: 11/10/-
Dil. Factor:	Date of Analysis:

Compound	MDL (ppbv)	Amount (ppbv)
Freon 12	0.5	Not Detected
Freon 114	0.5	Not Detected
Chloromethane	0.5	Not Detected
Vinyl Chloride	0.5	Not Detected
Bromomethane	0.5	Not Detected
Chloroethane	0.5	Not Detected
Freon 11	0.5	Not Detected
1,1-Dichloroethene	0.5	Not Detected
Freon 113	0.5	Not Detected
Methylene Chloride	0.5	Not Detected
1,1-Dichloroethane	0.5	Not Detected
cis-1,2-Dichloroethene	0.5	Not Detected
Chloroform	0.5	Not Detected
1,1,1-Trichloroethane	0.5	Not Detected
Carbon Tetrachloride	0.5	Not Detected
Benzene	0.5	Not Detected
1,2-Dichloroethane	0.5	Not Detected
Trichloroethene	0.5	Not Detected
1,2-Dichloropropane	0.5	Not Detected
cis-1,3-Dichloropropene	0.5	Not Detected
Toluene	0.5	Not Detected
trans-1,3-Dichloropropene	0.5	Not Detected
1,1,2-Trichloroethane	0.5	Not Detected
Tetrachloroethene	0.5	Not Detected
Ethylene Dibromide	0.5	Not Detected
Chlorobenzene	0.5	Not Detected
Ethyl Benzene	0.5	Not Detected
m,p-Xylene	0.5	Not Detected
o-Xylene	0.5	Not Detected
Styrene	0.5	Not Detected
1,1,2,2-Tetrachloroethane	0.5	Not Detected
1,3,5-Trimethylbenzene	0.5	Not Detected
1,2,4-Trimethylbenzene	0.5	Not Detected
1,3-Dichlorobenzene	0.5	Not Detected
1,4-Dichlorobenzene	0.5	Not Detected
Chlorotoluene	0.5	Not Detected
1,2-Dichlorobenzene	0.5	Not Detected
1,2,4-Trichlorobenzene	0.5	Not Detected
Hexachlorobutadiene	0.5	Not Detected

Container Type:

Surrogates:	% Recovery:	Method Limits:
Pentafluorotoluene:		70-130
Toluene-d8:		70-130
Bromofluorobenzene:		70-130

U.S. ENVIRONMENTAL PROTECTION AGENCY

CONTRACT LABORATORY PROGRAM

Volatile Organics in Ambient Air - Canister

EPA Sample No.

ANALYSIS DATA SHEET

Lab Name:		Contract:	SOW No.:
Lab Code:	Case No.:	SAS No.:	SDG No.:
lab Sample I.D.:		Date Received:	Date Analyzed:
Canister Pressure(units):	As Received:	( )	After Dilution: ( )
GC Column and I.D.:		Dilution Factor:	

CAS RN	COMPOUND	CONCENTRATION (ppbv)	Q
75-01-4	Vinyl chloride		
79-01-6	Trichloroethylene		
67-66-3	Chloroform		
71-43-2	Benzene		
56-23-5	Carbon Tetrachloride		
127-18-4	Tetrachloroethylene		
75-35-4	1.1-Dichloroethene		
107-13-1	Acrylonitrile		
107-06-2	1.2-Dichloroethane		
108-90-7	Chlorobenzene		
71-55-6	1.1.1-Trichloroethane		
79-06-5	1.1.2-Trichloroethane		
79-43-5	1.1.2.2-Tetrachloroethane		
100-41-4	Ethylbenzene		
75-09-2	Methylene chloride		
120-82-1	1.2.4-Trichlorobenzene		
100-42-5	Styrene		
75-34-3	1.1-Dichloroethane		
108-88-3	Toluene		
1330-20-7	Xylenes. m- & p-		
95-47-6	Xylene. o-		

Pace Analytical

Pace Analytical Services, Inc.

Printed on
Recycled Paper

LABORATORY
QUALITY ASSURANCE
PLAN

Pace Analytical Services, Inc. - Houston Laboratory

Approvals:

Quality Assurance Officer — Date: 10/30/96

Laboratory General Manager — Date: 10/30/96

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1. INTRODUCTION, PROGRAM OBJECTIVES, AND STATEMENT OF POLICY

1.1 INTRODUCTION

This Quality Assurance (QA) Plan is written in compliance with the elements required in the U.S. EPA, *Guidelines and Specifications for Preparing Quality Assurance Program Plans*, QAMS-005 80, December 1980. This document contains the required elements of a Quality Assurance Plan and is prepared in such a manner that entire sections can be referenced in subsequent specific project plans. This QA Plan shall be reviewed annually, at a minimum, by the Quality Assurance Officer and the laboratory management staff; revisions shall be incorporated as required.

The QA Plan defines the systems of quality control and quality assessment that constitute the comprehensive Quality Assurance program at the Pace Analytical Services, Inc.- Houston Laboratory (Pace-Houston). Quality control consists of specific procedures applied to all phases of analysis from sample receipt through the final reporting of results. The purpose of quality control is to ensure that quality goals are met under routine operating procedures. Quality assurance involves the continuous evaluation of data and monitoring of analytical processes for the purpose of ensuring that the quality control systems are performing effectively.

1.2 PROGRAM OBJECTIVES

The major elements of the Pace-Houston Quality Assurance Program are summarized as follow:

- Definition of the data quality objectives for the project.
- Use of appropriate methodologies by technically competent, well-trained personnel using sophisticated instrumentation and equipment to attain these objectives.
- Adherence to well-defined standard operating procedures with emphasis on good laboratory and measurement practices.
- Assessment of precision and accuracy by the use of quality control (QC) samples including, but not limited to, matrix spike samples, duplicate samples, surrogate spikes, blanks, and independent laboratory control standards.

- Use of the results of QC sample analyses for determining the measure of successful achievement of data quality objectives.

- Participation in external quality evaluation programs including the U.S. EPA Water Pollution (WP) and Water Supply (WS) Study Programs, client originated performance studies, and state agency certification programs.

- Maintenance of accreditation by state, federal, and other applicable agencies for work performed.

- Monitoring compliance with approved procedures and assessment of the performance of the analytical methods.

1.3 STATEMENT OF POLICY

Pace Analytical Services, Inc. expects from its management staff and all employees a high degree of commitment to quality assurance and to providing legally defensible data of known and appropriate quality to its clients. The validity and reliability of the information generated is optimized by the adherence to documented standard operating procedures (SOPs). Pace SOPs are written to comply the laboratory management's interpretation of the EPA-approved methods. SOPs used by Pace-Houston are also intended to comply with minimum requirements documents (MRDs), produced by Pace's corporate office to promote consistency and comparability between Pace laboratories.

Pace-Houston emphasizes the application of sound quality assurance/quality control principles beginning with the initial planning of the project, through all the field and laboratory activities and ultimately to the preparation of the final report. The principles of the data quality objectives for representativeness, completeness, comparability, precision, and accuracy are applied to the analytical data generated.

To ensure client satisfaction, Pace-Houston encourages strong interaction with the client at all phases of the project. Proactive interaction with the client assists Pace-Houston in delivering a final product that meets the project-specific data quality objectives.

Pace-Houston is committed to providing the resources, including facilities, equipment and personnel, to ensure the timely completion of analyses and adherence to applicable QA/QC protocols.

2. LABORATORY ORGANIZATION AND RESPONSIBILITY

Pace Analytical Services, Inc. operates a nationwide system of seven laboratories. Each laboratory is managed by a General Manager with responsibility for the technical and financial performance of the region. A centralized corporate staff provides support for the regional offices and coordination of inter-regional activities. This operational structure enables Pace to provide services which are responsive to the client's specific needs. It also provides a mechanism for each laboratory to utilize the total assets of the corporation to level work loads and provide a high-quality product in a timely manner.

Each laboratory is organized into departments, each headed by a Department Manager. In the Pace-Houston laboratory the technical departments are organic, inorganic, and field services. The departments of marketing and client services provides the client interface and project management staff necessary to ensure a project is completed in the manner required by the client. The department of support services provides the secretarial and accounting services necessary for operation of the laboratory. The Pace-Houston facility occupies a building of approximately 30,000 square feet; the floor plan is depicted in Figure 2-1.

Each laboratory has a Quality Assurance Officer (QAO) with responsibility for ensuring that all activities of the lab are in compliance with corporate policy for quality. The QAO reports directly to the General Manager and has the authority and the responsibility to implement and approve corrective actions as needed. The QAO is responsible for monitoring QC sample analysis results and the results obtained for analyses of external performance samples to identify potential problems. He is responsible for initiating both preventive and corrective action processes as needed to ensure proper operations within the laboratory. The QAO is also responsible for maintaining certifications required for laboratory operations.

Laboratory analysts are responsible for performing analyses according to standard operating procedures (SOPs) and for evaluating the acceptability of their data based on established quality control criteria. Analysts are also responsible for initiating corrective action when QC criteria are not met.

The organizational structure for Pace-Houston is provided in Figure 2-2. Job descriptions are on file with the laboratory personnel office for all analytical personnel. Job descriptions for specified functions will be made available upon request.

FIGURE 2-1

Pace Analytical Services, Inc. - Houston Laboratory Floor Plan

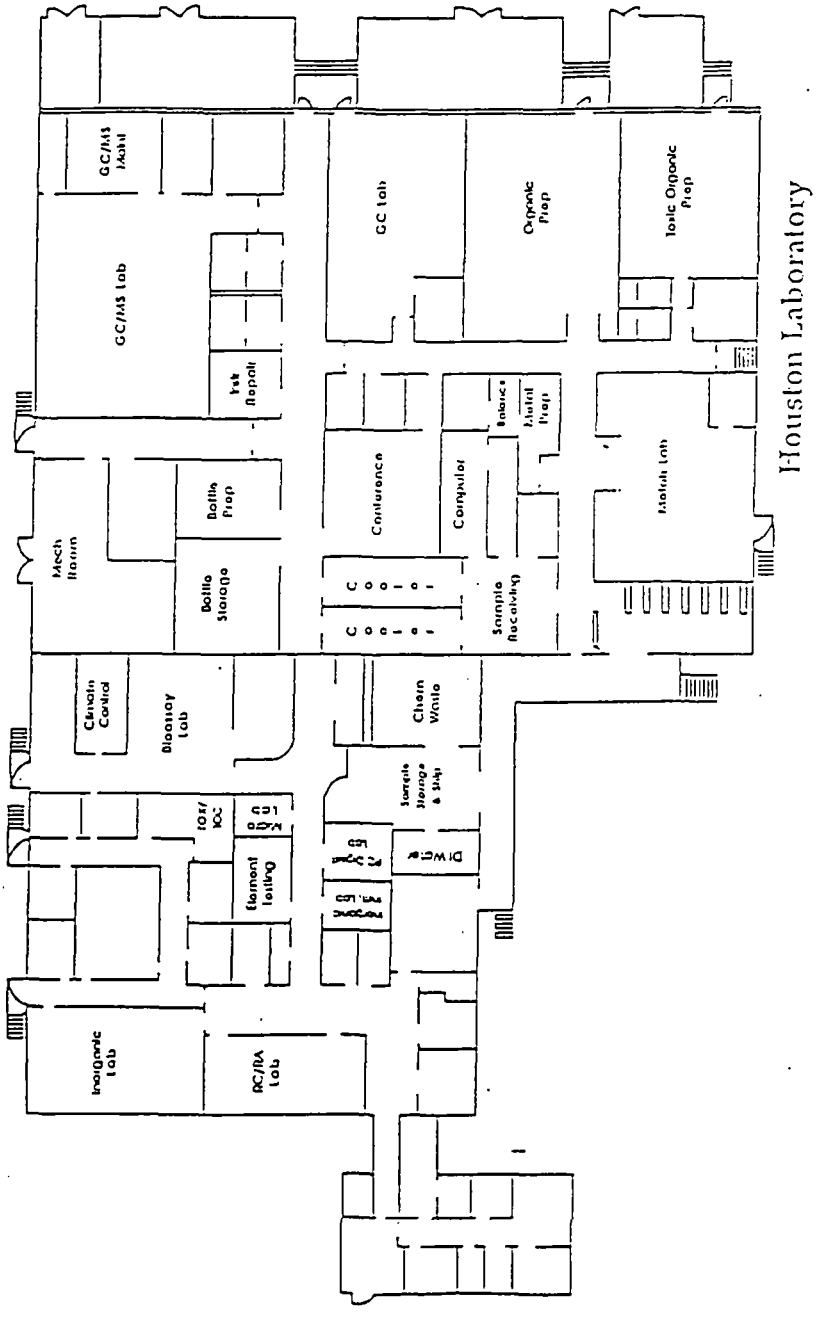
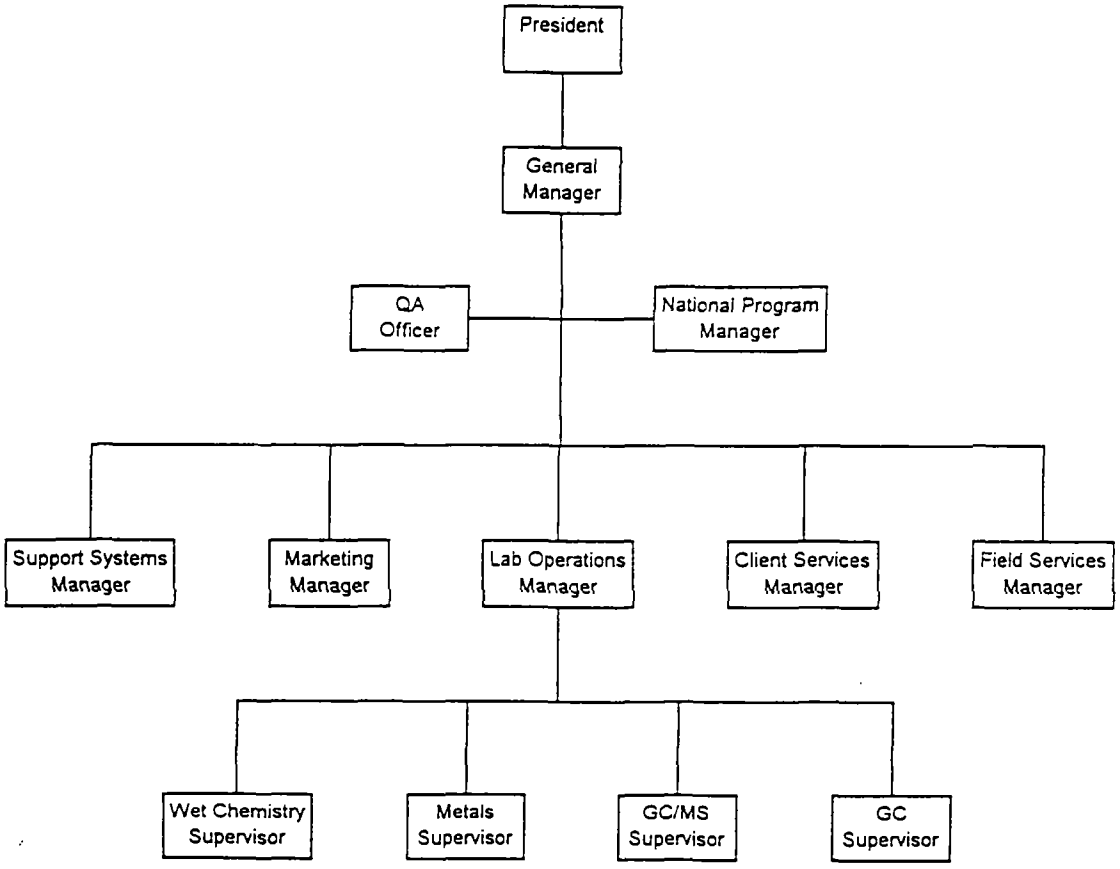


FIGURE 2-2

Pace Analytical Services, Inc. - Houston Laboratory Organization Chart



3. QUALITY ASSURANCE OBJECTIVES

3.1 INTRODUCTION

The purpose of this Quality Assurance Plan is to define procedures for the establishment of analytical systems and for the acquisition, documentation, evaluation, reporting, and archival of legally defensible data of known quality. The objective is to provide uniform systems for sample receipt, sample handling, instrument maintenance and calibration, methods control, performance evaluation, obtaining analytical data, evaluation of the quality of the data, and reporting. Specific procedures to be used for maintaining chain of custody, sample receipt and storage of samples, preventive maintenance, chemical analyses, internal quality control, reporting, QA audits, and corrective actions are described in specific sections of this plan or in standard operating procedures (SOPs) included by reference. This section addresses the objectives of accuracy, precision, completeness, representativeness, and comparability.

3.2 PRECISION AND ACCURACY

The QA objectives for precision and accuracy are to establish and maintain analytical systems that produce analysis results supported by QC data within acceptance criteria specified in the proposed analytical procedures. Precision and accuracy guidelines for the organic and inorganic procedures recommended by the USEPA are normally specified in the individual methods. These provide guidance as laboratory specific criteria are developed for each analytical method.

3.2.1 ORGANICS

Due to the extensive number of organic compounds selected as target analytes and environmental sample matrices, the development of precision and accuracy objectives and control limits for each analyte in all potential matrices is impractical. Thus, information is obtained for water and solid matrices that are representative of the normal environmental sample types. This is accomplished by determining the percent recovery of (1) matrix spike and matrix spike duplicate compounds added to selected samples before extraction and analysis, (2) surrogate spike compounds which are added to every sample, prior to extraction and analysis, and (3) laboratory control samples (LCSs), which are samples prepared from reference materials in DI water or clean sand and taken through the entire sample preparation and analysis procedure.

3.2.2 INORGANICS

Precision and accuracy data for inorganic test parameters are obtained by analyses of duplicate samples as a measure of precision and matrix spike and laboratory control samples as a measure of accuracy. At least one duplicate sample and matrix spike sample are analyzed per sample matrix type (e.g. water, soil) and concentration (e.g. low, medium) per batch of samples or for each 10 samples analyzed, whichever is more frequent, or as specified by project requirements. Samples identified as field blanks can not be used for matrix spike/duplicate sample analysis. If two analytical methods are used to obtain the reported values for the same element for a batch of samples (i.e. ICP, GFAA), matrix spike/duplicate samples are analyzed by each method. The matrix spike recovery and relative percent difference (RPD) of the duplicates for each component is calculated for data assessment. The method of standard additions (MSA) is employed, where applicable to the specific method performed, in order to achieve accuracy when matrix interferences are present in a sample.

3.2.3 FIELD SAMPLING

Field blanks and duplicates are collected and analyzed to assess field sampling activities. The analytical results for these samples provide data indicating procedural contamination, ambient conditions at the site, and representativeness of the analysis sample.

3.3 COMPLETENESS

Completeness is a measure of successfully obtaining all information necessary for a valid scientific study. The objective for completeness is: The methodology proposed for chemical characterization of the samples collected will provide data meeting QC acceptance criteria, following standard laboratory data review and validation, for at least 95% of all samples collected. Completeness may also be defined as a comparison of the number of tests successfully completed (with acceptable QC) to the number of tests requested. Nonconformance/corrective action (NC/CA) records are completed in accordance with standardized procedures in order to provide explanation when QC criteria are not met. The NC/CA record is completed by the analyst describing the situation encountered. The corrective action required is taken and documented in the appropriate section of the NC/CA record by the supervisor and analyst. See Section 13, Corrective Action.

3.4 REPRESENTATIVENESS

Representativeness is a qualitative measure that is related to the ability to obtain a sample that best reflects the characteristics of that part of the environment that is to be assessed. The laboratory utilizes homogenization of the sample, if compatible with the tests to be performed, to ensure the results obtained are representative of the sample as received.

3.5 COMPARABILITY

Comparability is also considered during preparation of the work plan. The objective of comparability is to produce results that do not differ significantly from those produced by other parties for the same purpose. Pace-Houston uses SOPs based on EPA-approved methods in order to achieve comparability with data from previous studies and from other laboratories. SOPs are written to incorporate the method requirements specified by the Pace corporate office in minimum requirements documents (MRDs), thus promoting comparability within the Pace system of laboratories. If an EPA-approved procedure is not available or not required for the analyte(s) or matrix to be analyzed, alternative published and/or validated procedures are submitted for client review and approval prior to analyses of samples.

Pace-Houston participates in external and inter-laboratory performance evaluation (PE) studies as an additional means of establishing comparability in the laboratory. Pace-Houston participates in USEPA Water Pollution (WP) and Water Supply (WS) studies, USEPA DMR-QA studies, and PE programs for various state and federal agencies and commercial clients. Pace-Houston also periodically analyzes single-blind QC check samples in order to internally monitor performance of parameters which are not evaluated by external PE studies.

4. SAMPLING PROCEDURES

4.1 PURPOSE AND APPLICABILITY

This procedure establishes requirements for the preservation of samples and the collection of samples by Field Services Department at Pace-Houston.

4.2 RESPONSIBILITIES

4.2.1 FIELD TECHNICIANS

Field Technicians are responsible for the collection of samples and for documentation of each sampling event in accordance with this procedure. Field Technicians are also responsible for field equipment decontamination and maintenance.

4.2.2 FIELD SUPERVISOR

The Field Supervisor is responsible for training field technicians and supervising their work, including review of sampling documentation and field reports. The supervisor is the on-site team leader for major projects.

4.2.3 FIELD MANAGER

The Field Manager is responsible for work plan and safety plan development. The Field Manager is also responsible for adherence to all quality assurance and regulatory guidelines.

4.2.4 SAMPLE CUSTODIANS

The Sample Custodians are responsible for storing samples and retrieving them from storage. Sample Custodians also add preservatives to sample containers, ship them to clients, and verify preservation of samples upon receipt at the laboratory.

4.2.5 SAMPLE COURIER

The sample courier is responsible for accepting samples under chain-of-custody from clients and samplers at field locations.

4.2.6 LABORATORY DEPARTMENT MANAGERS

The Laboratory Department Managers are responsible for scheduling sample analyses to ensure that holding times are met.

4.3 PROCEDURE

4.3.1 MATERIALS

a. Sample Containers

Sample containers are constructed of polyethylene or glass, as listed on Tables 4-1, 4-2, and 4-4. Pace-Houston routinely uses new sample containers obtained from a supplier that has been qualified, by the laboratory's analysis of DI water bottle blanks, to deliver containers free from contamination. Sample containers are used once only and disposed of according to federal, state, and local guidelines. In addition, Pace-Houston can supply certified, precleaned bottles upon request. Sample containers are stored in an area free of contamination.

b. Sample Preservation

Sample preservation techniques and holding times for non-CLP work are listed in the following tables:

- Table 4-1 – NPDES, NPDWR, and Aqueous RCRA Samples
- Table 4-2 – Non-Aqueous RCRA Samples
- Table 4-3 – Samples undergoing TCLP
- Table 4-4 – CLP Samples

The reagents and glassware used to prepare chemical preservatives are segregated and used only to prepare preservatives. To verify freedom from contamination, a preservative blank is analyzed each time a new manufacturer's lot of reagent is used to prepare the preservative. The blank is analyzed prior to use of the new preservative.

Preservatives are added directly to the sample containers. Labels indicating the type of preservative and the date of preparation are placed on eachsample container. A log of sample bottle preparation is maintained, which lists the type and number of bottles prepared, the preservatives used (including manufacturer and lot number of reagents), the date, and the preparer. Refer to Pace SOP number HO-P-002, *Sample Storage, Tracking, and Bottle Preparation*, for detailed procedures for sample container preparation.

c. Sample Bottle Orders

- Bottle orders specifying the following information are prepared by the Project Manager on a bottle order (Figure 4-1) or equivalent. Bottle orders must be placed as far in advance as possible.

  - Analyses, matrices, and number of samples
  - EPA program (RCRA, NPDES, NPDWR, etc.)
  - Name and address if bottles are to be delivered
  - Date required (this should be at least one day before sampling, so that if the client requires additional bottles, they can be sent).
  - Mode of transportation to the sampling site.

  The bottle order should also request chain-of-custody procedures (chain-of-custody record, Figure 4-2 or equivalent, and custody seals on coolers), trip blanks, etc. when required for the project.

- Trip blanks are prepared by completely filling a 40-mL VOA vial with organic-free reagent water, pouring the water down the side of the vial to minimize turbulence. The last few drops are gently poured into the vial so that surface tension holds the water in a convex meniscus. The vial is then capped. If air space is present, repeat the procedure. The vial is labeled as a trip blank. Preserved and unpreserved vials are prepared for each blank.

Preparation of field blanks is dependent on their function. The specific purpose of a field blank is discussed with the client when the order for bottles is placed. Preparation instructions are then specified by the Project Manager on bottle order or in a project-specific work plan or quality assurance plan.

- The bottle order is filled by a Sample Custodian. Bottles, with proper preservatives added, are packed in shipping containers in a manner that minimizes breakage. If the sampling event includes perishable parameters, the bottles must be packed in thermal coolers. A temperature blank bottle is added to each cooler to allow the Sample Custodian to accurately record the cooler temperature when samples are later received.

- A chain-of-custody form is sealed in a plastic bag and sent with each bottle order to encourage clients to complete the form and return it with the samples

The bottles may be picked up at the laboratory, delivered by Pace to the site, or delivered by a third party carrier.

4.3.2 SAMPLE COLLECTION BY FIELD SERVICES

a. Sampling Procedures

The sampling procedures used by Pace-Houston Field Services are outlined in the following manuals:

- Test Methods for Evaluating Solid Waste, Volume II: Field Manual Physical/Chemical Methods, SW-846, November 1986, and updates.

- Handbook for Monitoring Industrial Wastewater, Chapter 6, U.S. EPA Technology Transfer, August 1973.

- Handbook for Sampling and Sample Preservation of Water and Wastewater, EPA-600/4-82-029.

- Groundwater Monitoring Technical Enforcement Guidance Document, EPA, September 1986.

b. Field Notes

Field notes are documented in bound laboratory notebooks or on prenumbered field forms that are later bound into books. The following information is documented for each sampling event, at a minimum.

- For each event:
  - Location of sampling event.
  - Identification and calibration, where appropriate, of equipment used in sampling or in taking field measurements.
  - Weather conditions.
  - Description of anomalies at the site.
  - Signature of sample collector.
- For each sample:
  - Sample matrix (groundwater, wastewater, soil, sludge, oil, etc.).
  - Type of sample (composite or grab).
  - Location of the sampling point.
  - Date and time of sample collection.
  - Field measurements.

Field notes must be filed chronologically by site. Field notes will be reviewed for completeness and appropriateness by the Field Supervisor or senior Field Technician prior to report preparation.

c. Chain-of-Custody Record

A chain-of-custody record (Figure 4-2 or equivalent) should be completed for each sampling event to document sample custody from the time of collection through transfer of custody to the laboratory. At a minimum, the chain-of-custody record must contain the following information.

- Analyses required
- Type of sample bottle (e.g., metals, water chemistry, cyanide).
- Sample identification.
- Signature of collector.
- Date and time of sample collection.
- Signature and inclusive dates and times of possession for each person taking custody of the samples.

d. Field Measurements

When requested, the following measurements must be made in the field at the time of sample collection because of holding time limitations:

- Residual chlorine
- pH
- Dissolved oxygen
- Sulfite
- Temperature

e. Sample Delivery to the Laboratory

Samples must be delivered to the laboratory in a manner such that the characteristics of the sample are preserved and the analyses can be completed within the holding times.

4.3.3 SAMPLE PICK-UP BY PACE

At sample pick-up, the Pace driver requests a completed chain-of-custody record or release document with the samples. The driver signs and dates the chain-of-custody record or release document.

- Location of the sample pick-up (company and plant name).
- Date and time of pick-up.
- Driver's signature.

If the client does not provide a chain-of-custody record or release document, the driver completes a chain-of-custody record with the following information and obtains the signature (along with the date and time) of the client representative relinquishing custody of the samples:

- Client (company) name and location.
- Sample identification of each sample if they are not in sealed shipping containers. If the samples are sealed in shipping containers, the number of shipping containers is noted in the comments portion of the form.
- The driver also signs the form (along with the date and time) signifying receipt of the samples.

4.4 RECORDS

The following records are maintained in support of this procedure:

- Sampling notes
- Chain-of-custody records
- Field duplicates data
- Bottle preparation logs

FIGURE 4-1
BOTTLE ORDER FORM

pace INCORPORATED
ENVIRONMENTAL LABORATORIES

900 Gemini Avenue
Houston, TX 77058
713-488-1810
FAX: 713-488-4661

BOTTLE ORDER FORM

(ONE ORDER PER SHIPMENT)

Project Mgr: _____

SHIP TO: (SHIPPING ADDRESS ONLY)
COMPANY: _____
ADDRESS: _____
CITY: _____ STATE: ____ ZIP: _____
ATTN: _____
PHONE: _____
OTHER CONTACT: _____

DATE OF ORDER: _____
DUE DATE: _____
SPECIAL INSTRUCTIONS: _____

CHECKED BY: _____
DATE CHECKED: _____
CTNS IN SHIPMENT: _____
TOTAL WT: _____
SHIPPED VIA _____
DATE SHIPPED: _____
AIR BILL: _____
BILL CLIENT:
ALICUNT: S _____
SHIPPER'S INITIALS: _____

ALL BOTTLE ORDERS INCLUDE PACE CHAIN OF CUSTODY FORMS, BOTTLE LABELS, CUSTODY SEALS AND SAMPLING INSTRUCTIONS

Individual Bottles

Plastic w/ Poly-cone Caps			Glass w/ Aluminum & Teflon Lined Caps			
Water Chemistry	___qt	___pt	TOX (H_2SO_4)(Amber)		___qt	___8 oz
BOD	___qt		Organics	___gal	___1/2 gal	___qt
Metals (w/ HNO_3)	___qt	___pt	PCX (2 X 40 ml septum vial/pkg)		___pkg	
(wo/ HNO_3)	___qt	___pt	VOA (2 X 40 ml septum vial/pkg; w/HCL)		___pkg	
Nitrogen (H_2SO_4)	___qt	___pt	VOA (2 X 40 ml septum vial/pkg; wo HCL)		___pkg	
COD (H_2SO_4)	___8 oz	___4 oz	VOA (3 X 40 ml septum vial/pkg; w/HCL)		___pkg	
TOC (H_2SO_4)	___8 oz	___4 oz	Solids (wide mouth jar)		___qt	___pt
Cyanide (NaOH)	___qt				___8 oz	___4 oz
Sulfide (NAOH, ZNCAC)	___pt		Soil VOAs		___4 oz septum vial	
Bacteria (Stanle:$Na_2S_2O_3$)	___8 oz					
Radiochemistry (HNO_3)	___gal					

Amber Glass w/ Poly-cone Caps		
Oil & Grease (HCL)	___qt	
TPH (HCL)	___qt	
Phenolics (H_2SO_4)	___qt	___pt

Miscellaneous	
Empty Ice Chests	___
Ice Packs (freeze gels)	___
Temperature Blank	✓
Other (specify)	

Prepared Bottle Kits

NPDES Kits		Appendix IX Sampling Kit	
Composite Sample		___Organics (3 X 1 gal)	___Metals (1 qt)
___BOD (1 qt)	___Water Chem (1 qt)	___VOA sets (3 X (2 X 40 ml))	
___Cyanide (1 qt)	___Metals (1 qt) w/ HNO_3	___Cyanide (1 qt)	___Sulfide (1 pt)
___Phenolics (1 qt)	___Sulfide (1 pt)		
___Organics (1 gal)	___Radiochem (1 gal)		
___Nitrogen (1 qt)			
Grab Sample			
___Bacteria (4 X 8 oz)	___(8 oz)		
___Oil & Grease (4 X 2 qt)	___(1 qt)		
___VOA (8 X (2 X 40 ml)) w/ HCL	___(2 X 40 ml) w/ HCL		
___Field Blank (2 X 40 ml vails, filled with organic-free DI water)			

Field & Trip Blanks	
VOA Field Blank	___pkg ___w/ HCL ___wo/ HCL
(2 X 40 ml septum vials, empty; supplied w/ organic-free DI water)	
VOA Trip Blank	___pkg ___w/ HCL ___wo/ HCL
(2 X 40 ml septum vials, filled w/ organic-free DI water)	
Other (specify)	

Waste Characterization Kit	Sampling Kits
___TCLP & ZHE: (1 qt WM jar and 4 oz vial)	___Transformer Oil (2 oz bottle)
___TCLP (only): 1 qt WM jar	___PCB Wipe (4 oz metal can)
___Aqueous TCLP & ZHE: (1 gal & 2 X 40 ml vials wo/ HCL)	___Stormwater grab ___ comp ___
___RCI: 1 qt WM jar	

WHITE — PACE SHIPMENT RECORD
YELLOW — CLIENT
PINK — WORK ORDER QUOTE SHEET

FIGURE 4-2
FIELD CHAIN-OF-CUSTODY RECORD

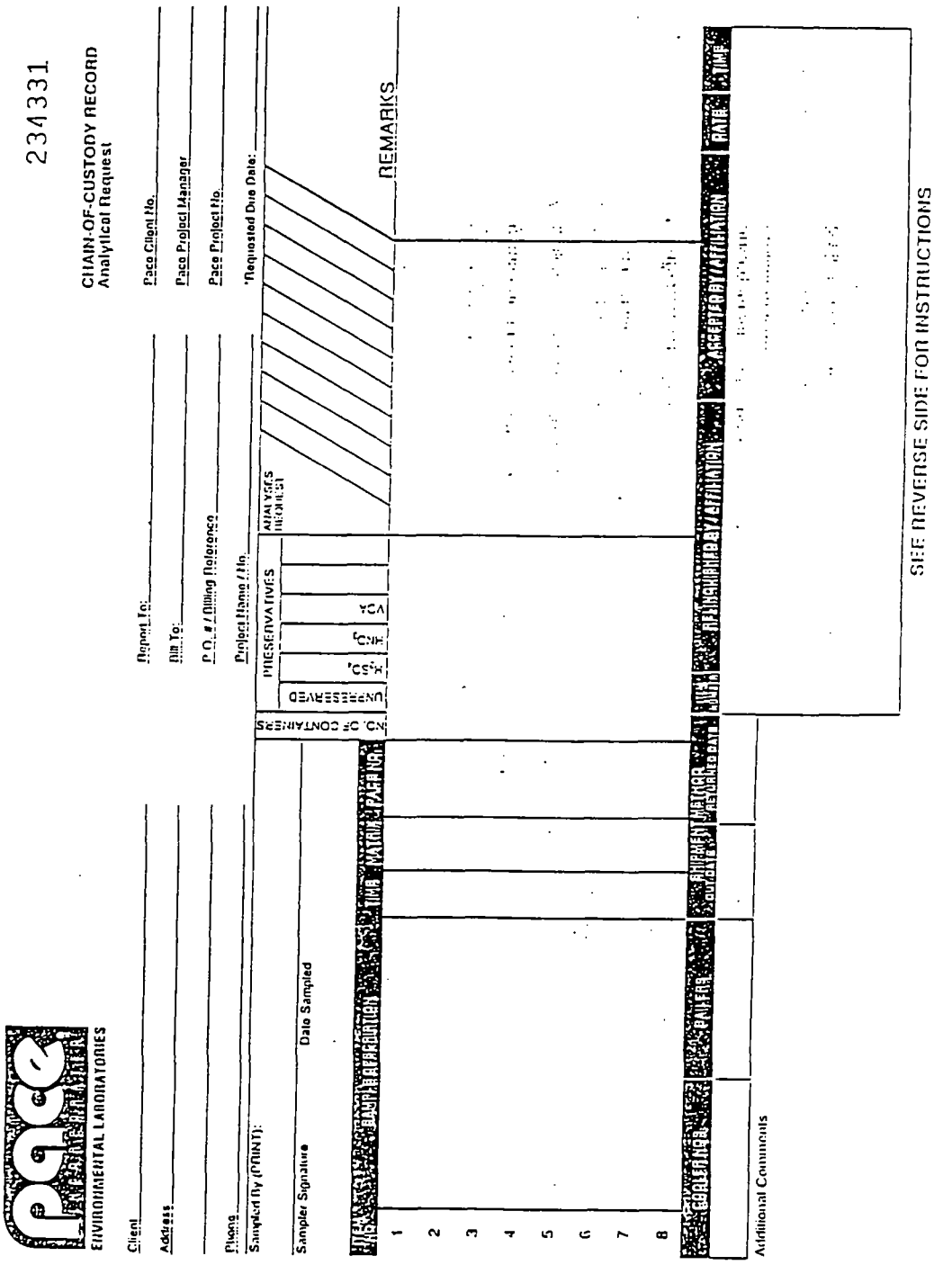


TABLE 4-1

Container, Preservation and Holding Time Requirements Aqueous Samples - Non-CLP Work

Parameter	Container[1]	Preservative[2][5]	Maximum Holding Time[3]
Acidity	P, G	Cool, 4°C	14 days
Alkalinity	P, G	Cool, 4°C	14 days
BOD	P, G	Cool, 4°C	48 hours
Boron	P	HNO_3 to pH <2	6 months
Bromide	P, G	None	28 days
Chloride	P, G	None	28 days
Chlorine, Residual	P, G	None	Analyze Immediately
Chromium, Hexavalent	P, G	Cool, 4°C	24 hours
COD	P, G	Cool, 4°C; H_2SO_4 to pH <2	28 days
Color	P, G	Cool, 4°C	48 hours
Cyanide, Total and Amenable to Chlorination	P, G	Cool, 4°C; NaOH to pH >12[4]	14 days
Dissolved Oxygen			
by Probe	G bottle and top	None	Analyze Immediately
by Winkler Titration	G bottle and top	Fix on site and store in dark	8 hours
Fluoride	P	None	28 days
Hardness	P, G	HNO_3 to pH <2	6 months
Iodide	P, G	Cool, 4°C	28 Days
MBAS	P, G	Cool, 4°C	48 hours

Parameter	Container[1]	Preservative[2][5]	Maximum Holding Time[3]
Mercury	P, G	HNO_3 to pH <2	28 days
Metals, except Boron, Cr^{6+}, and Mercury	P, G	HNO_3 to pH <2	6 months
Nitrogen			
Ammonia	P, G	Cool, 4°C; H_2SO_4 to pH <2	28 days
Kjeldahl, Total	P, G	Cool, 4°C; H_2SO_4 to pH <2	28 days
Nitrate-Nitrite	P, G	Cool, 4°C; H_2SO_4 to pH <2	28 days
Nitrate	P, G	Cool, 4°C	48 hours
Nitrite	P, G	Cool, 4°C	48 hours
Odor	G, w/TLC	None	24 hours
Oil and Grease	G, w/TLC	Cool, 4°C; HCl to pH <2	28 days
Organic Carbon	P,G	Cool, 4°C; H_2SO_4 to pH <2	28 days
Petroleum Hydrocarbons, Total	G, w/TLC	Cool, 4°C; HCl to pH <2	28 days
pH	P, G	None	Analyze Immediately
Phenolics	G, w/TLC	Cool 4°C; H_2SO_4 to pH <2	28 days
Phosphorus			
Elemental	G, w/TLC	Cool, 4°C	48 hours
Hydrolyzable	P, G	Cool, 4°C; H_2SO_4 to pH <2	48 hours

Parameter	Container[1]	Preservative[2][5]	Maximum Holding Time[3]
Orthophosphate	P, G	Filter immediately; Cool, 4°C	48 hours
Phosphorus, Total	P, G	Cool, 4°C; H_2SO_4 to pH <2	28 days
Solids			
Dissolved	P, G	Cool, 4°C	7 days
Total	P, G	Cool, 4°C	7 days
Suspended	P, G	Cool, 4°C	7 days
Settleable	P, G	Cool, 4°C	48 hours
Volatile	P, G	Cool, 4°C	7 days
Silica	P	Cool, 4°C	28 days
Specific Conductance	P, G	Cool, 4°C	28 days
Sulfate	P, G	Cool, 4°C	28 days
Sulfide	P, G	Cool, 4°C; Zinc acetate + NaOH to pH >9	7 days
Sulfite	P, G	None	Analyze Immediately
Temperature	P, G	None	Analyze Immediately
TOX	AG w/TLC	Cool, 4°C, H_2SO_4 to pH <2	28 days
Turbidity	P, G	Cool, 4°C	48 hours
BACTERIOLOGICAL TESTS			
Coliform, Fecal and Total	P, G sterile	Cool, 4°C[7]	6 hours
Fecal Streptococci	P, G sterile	Cool, 4°C[7]	6 hours

Parameter	Container[1]	Preservative[2][5]	Maximum Holding Time[3]
ORGANIC CHEMISTRY TESTS[6]			
Acrolein and Acrylonitrile	G with TLS	Cool, 4°C[7]; pH 4-5	14 days
Purgeable Halocarbons	G with TLS	Cool, 4°C[7]	14 days
Purgeable Aromatics	G with TLS	Cool, 4°C[7]; HCl to pH <2	14 days
Trihalomethanes/ VOCs	G with TLS[8]	Cool, 4°C; $Na_2S_2O_3$[9] (RCRA - HCl to pH <2)	14 days (NPDES - 7 days if not preserved with HCl)
Benzidines	G with TLC	Cool, 4°C[7]	7 days until extraction, 7 days after extraction
Chlorinated Hydrocarbons	G with TLC	Cool, 4°C	7 days until extraction, 40 days after extraction
Haloethers	G with TLC	Cool, 4°C[7]	7 days until extraction, 40 days after extraction
Nitroaromatics and Isophorone	G with TLC	Cool, 4°C[7]; store in dark	7 days until extraction, 40 days after extraction
Nitrosamines	G with TLC	Cool, 4°C[7]	7 days until extraction, 40 days after extraction
PCBs	G with TLC	Cool, 4°C	7 days until extraction, 40 days after extraction
Pesticides	G with TLC	Cool, 4°C; pH 5-9	7 days until extraction, 40 days after extraction
Phenols	G with TLC	Cool, 4°C[7]	7 days until extraction, 40 days after extraction
Phthalate Esters	G with TLC	Cool, 4°C	7 days until extraction, 40 days after extraction
Polynuclear Aromatic Hydrocarbons	G with TLC	Cool, 4°C[7]; store in dark	7 days until extraction, 40 days after extraction

Parameter	Container[1]	Preservative[2][5]	Maximum Holding Time[3]
TCDD	G with TLC	Cool, 4°C[7]	7 days until extraction, 40 days after extraction
Herbicides	G with TLC	Cool, 4°C	7 days until extraction, 40 days after extraction
RADIOCHEMISTRY TESTS			
Gamma Spectrometry	P, G	HNO_3 to pH <2	
Gross Alpha	P, G	HNO_3 to pH <2	6 months
Gross Beta	P, G	HNO_3 to pH <2	6 months
Iodine 131	P, G	None	3 weeks
Radium	P, G	HNO_3 to pH <2	6 months
Strontium	P, G	HNO_3 to pH <2	
Tritium	P, G[10]	None	
Uranium	P, G	HCl to pH <2	
AQUATIC TOXICITY TESTS			
Chronic Tests	P, G	Cool, 4°C	36 hours
Acute and Serial	P, G	Cool, 4°C	72 hours

TABLE 4-1 NOTES

1. AG - amber glass
   G - glass
   P - polyethylene
   TLC - teflon-lined cap
   TLS - teflon-lined septum

2. Sample preservation should be performed immediately upon sample collection. For composite samples, samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

3. The holding times listed are the maximum times that samples may be held before analysis and still be considered valid under EPA regulations. Holding times are measured from date of sampling.

4. Add 0.6 g ascorbic acid if residual chlorine is present.

5. If the dissolved content is to be measured, samples should be filtered on site immediately before adding preservatives.

6. When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times should be observed for optimum safeguard of sample integrity. When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to 4°C, reducing residual chlorine (if present) with 0.008 percent sodium thiosulfate, storing int he dark, and adjusting the pH to 6-9; samples preserved in this manner may be held for 7 days before extraction and for 40 days after extraction. Exceptions to this optional preservation and holding time procedure are:

   - 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0 ± 0.2 to prevent rearrangement to benzidine.

   - Extracts may be stored up to 7 days before analysis for benzidines if storage is conducted under an inert (oxidant-free) atmosphere.

7. Add $Na_2S_2O_3$ if residual chlorine is present (0.008 percent).

8. Samples are to be collected in duplicate; provide two vials per sample. Also provide duplicate trip blanks for each sample set.

9. Omit $Na_2S_2O_3$ if maximum trihalomethane potential is to be determined.

10. New Jersey DEP requires that samples be collected in glass only for work performed in that state.

These requirements are based on 40 CFR 136, Table II; SW-846, Third Edition, Revision 2, Table 2-33; and EPA 814B-92-002, Table IV-4 and IV-5.

TABLE 4-2

Container, Preservation and Holding Time Requirements Non-Aqueous Samples - Non-CLP Work

Parameter	Container[1]	Preservative[2][6]	Maximum Holding Time[3]
Volatile Organics			
Concentrated Waste	8 oz. wide-mouth glass with TLC	None	14 days
Soil/Sediment	8 oz. wide-mouth glass with TLC	Cool, 4°C	14 days
Sludge	8 oz. wide-mouth glass with TLC	Cool, 4°C	14 days
Semi-Volatile Organics			
Concentrated Waste	8 oz. wide-mouth glass with TLC	None	14 days until extraction, 40 days thereafter
Soil/Sediment	8 oz. wide-mouth glass with TLC	Cool, 4°C	14 days until extraction, 40 days thereafter
Sludge	8 oz. wide-mouth glass with TLC	Cool, 4°C	14 days until extraction, 40 days thereafter
Metals			
All except mercury	8 oz. wide-mouth glass with TLC	Cool, 4°C	6 months
Mercury	8 oz. wide-mouth glass with TLC	Cool, 4°C	28 days

1. TLC = teflon-lined cap.

2. Soil/sediment and sludge samples should be cooled to 4°C for all parameters.

3. The holding times listed are the maximum times that samples can be held before analysis and still be considered valid under EPA regulations. Holding time is measured from sampling.

TABLE 4-3

Holding Time Requirements for Samples Undergoing Toxicity Characteristic Leaching Procedure (TCLP)

Analysis	From field collection to TCLP extraction	From TCLP extraction to preparative extraction	From preparative extraction to analysis	Total elapsed time
Volatiles	14 days	N/A	14 days	28 days
Semivolatiles	14 days	7 days	40 days	61 days
Mercury	28 days	N/A	28 days	56 days
Metals (ex. Hg)	180 days	N/A	180 days	360 days

TABLE 4-4

Container, Preservation and Holding Time Requirements CLP Work

Parameter	Container[1]	Volume	Preservative[2,3]	Maximum Holding Time[4]
Metals except Hg	Aqueous: P with PLC	1000 mL	HNO_3 to pH <2	6 months
	Non-Aqueous: G with TLC	4-32 oz.	Cool, 4°C	6 months
Hg	Aqueous: P with PLC	1000 mL	HNO_3 to pH <2	26 days
	Non-Aqueous: G with TLC	4-32 oz.	Cool, 4°C	26 days
Cyanide	Aqueous: P with PLC	1000 mL	NaOH to pH >12; Cool,4°C	12 days
	Non-Aqueous: G with TLC	4-32 oz.	Cool, 4°C	12 days
Volatile Organics	Aqueous: G with TLS	2-40 mL vials	Cool, 4°C; Dark	10 days
	Non-Aqueous: G with TLC	4 oz.	Cool, 4°C; Dark	10 days
Semi-volatile Organics, Pesticides/PCBs	Aqueous: AG with TLC	1/2 Gal.	Cool, 4°C; Dark	5 days until extraction[6]; 40 days thereafter
	Non-Aqueous: AG with TLC	8-16 oz.	Cool, 4°C; Dark	10 days until extraction[6]; 40 days thereafter

TABLE 4-4 NOTES

1. AG = Amber glass
   G = Glass
   P = Polyethylene
   PLC = Polyethylene-lined cap
   TLC = Teflon-lined cap
   TLS = Teflon-lined septa

2. Sample preservation should be performed immediately upon sample collection. For composite samples, samples may be preserved by maintaining at 4°C until compositing and sample splitting are complete.

3. If the dissolved content is to be measured, samples should be filtered on-site immediately before adding preservatives.

4. The holding times listed are the maximum times that samples may be held before analysis and still be considered valid under EPA regulations. Holding times are measured from the verified time of sample receipt (TVSR) at the laboratory. (Holding time in the field must be minimized when organics and/or cyanide are parameters of interest.)

5. If residual chlorine is present, all 0.6 g ascorbic acid.

6. Separatory and sonication extraction procedures must be completed within the holding time. Continuous extraction procedures (applicable to aqueous samples only) must be started within the holding time.

5. SAMPLE CUSTODY

5.1 SAMPLE RECEIPT AND VERIFICATION

All samples received by the Pace-Houston laboratory are accompanied by a chain-of-custody form completed by the client and/or sampler. Pace Analytical Services, Inc. provides chain-of-custody forms for all containers supplied to the client. Figure 4-2 shows the Pace chain-of-custody form. Clients choosing to utilize chain-of-custody forms other than those provided by Pace are responsible for ensuring all essential information is included on the form used.

Samples are received in accordance with the procedures set forth in Pace SOP number HO-P-001, *Sample Receipt and Log-in*. Shipping containers are inspected for custody seals and the condition is noted in the sample receipt log. The shipping containers are then opened and inspected for enclosed documentation. The temperature inside the shipping container is determined and recorded on the chain-of-custody form. The sample bottles are inspected for breakage and/or evidence of leakage. The sample bottle labels are inspected and compared to the chain-of-custody. The pH of preserved aqueous samples is verified as soon as possible after sample receipt.

The chain-of-custody is compared to the Project Alert Form provided by the Pace Project Manager. Any discrepancy noted is described on a nonconformance/ corrective action (NC/CA) record (see Figure 13-1) and the Pace Project Manager is notified immediately. The Project Manager is responsible for contacting the client and determining the corrective action required. The action taken is recorded on the NC/CA record and maintained in the project file.

5.2 SAMPLE LOG-IN

Samples are logged into the Pace-Houston Laboratory Information Management System (LIMS) in accordance with the LIMS User's Manual and Pace SOP number HO-P-001, *Sample Receipt and Log-in*.

Upon entry of all required sample tracking and analysis information into the LIMS, the information is reviewed by the Pace Project Manager for accuracy and completeness. Any errors or omissions are corrected at this time.

5.3 SAMPLES RECEIVED WITH NO PAPERWORK

Samples received with no paperwork are held in refrigerated storage in the sample receiving area until the proper instructions for analysis are received. The client is contacted immediately and the resolution of the problem is documented in the project file.

5.4 SAMPLE STORAGE

The sample containers are stored in designated refrigerators according to the type of analyses to be performed. Sample storage locations are listed in Pace SOP number HO-P-002, *Sample Storage, Tracking and Bottle Preparation*. Samples to be analyzed for volatile organic compounds are stored in separate refrigerators designated for volatile samples. Samples requiring strict internal chain-of-custody (direct tracking) are kept in locked storage areas. All refrigerators are monitored daily by a designated member of the Sample Custodian staff to ensure the temperature is maintained within a range of 2-6°C. Deviations from this temperature range are noted in the temperature logbook and corrective action is taken immediately to ensure the integrity of the samples.

5.5 SAMPLE/DATA ACCESS AND INTERNAL CHAIN-OF-CUSTODY

Pace follows standard operating procedures to assure the integrity of samples, prevention of degradation, and to prevent disclosure of data to unauthorized personnel. In order to ensure that this policy is maintained, the laboratory facilities are operated under controlled access. Only employees are allowed into the laboratory. Visitors must register upon arrival and are allowed access to the facility only with an escort.

Policies and procedures for maintaining internal chain-of-custody of samples are contained in Pace SOP number HO-P-002, *Sample Storage, Tracking, and Bottle Preparation*. Samples requiring strict internal chain-of-custody are signed in and out of locked storage areas by sample custodians and analysts.

5.6 SAMPLE DISPOSITION

Samples not totally consumed during analysis and any excess extracts or digestates generated during sample analysis are disposed of in accordance with local, state, and federal regulations. Specific disposal requirements are arranged with the client prior to receipt of samples. Client stipulated disposition requirements are to be set forth in the contract. Sample disposal is described in Pace SOP number HO-P-007, *Laboratory Waste Disposal and Sample Disposition*.

6. CALIBRATION PROCEDURES AND FREQUENCY

Analytical instruments and equipment used to obtain measurements or record data to be used for calculations of analytical results are calibrated at a frequency and in a manner such that accuracy and reproducibility are consistent with the manufacturer's specifications for proper instrument operation, and the calibration is in compliance with the analysis method requirements.

Laboratory measurements are based upon comparisons to results obtained for the analyses of reference standards analyzed by the same method. The results obtained for the analyses of calibration standards are used to prepare calibration curves or calculate calibration factors. The results of the sample analyses are quantified using either internal or external calibration techniques. Typically calibration is achieved by the analyses of five calibration standards at concentration levels set forth in the referenced method.

All instruments are calibrated using standard solutions of known concentrations. Where available, the standards are prepared from certified reference materials traceable to NIST or from reference materials whose concentration has been verified against NIST-traceable materials. Calibration standards are routinely verified for accuracy immediately following calibration and throughout the analytical sequence by using second-source standards. Thermometers and balances are calibrated annually using NIST-traceable thermometers and weights. Daily verification of balance calibration is described in Pace SOP number HO-P-003, *Calibration Verification of Laboratory Balances*.

Calibration standards are prepared from commercially available traceable stock standard solutions. The identity of the stock solution, preparation procedure, date, preparer, expiration date, and identity of the calibration standard are recorded in a standards preparation logbook. The entry is dated and signed by the preparation analyst.

The laboratory calibration procedures utilized must meet or exceed the method calibration criteria for all analyses performed. In the event that calibration criteria are not met, scientific justification to proceed with analysis is provided by the analyst. Supervisor and QAO approval must be obtained, or appropriate corrective action taken prior to analysis of samples. The calibration procedure in the method is followed for each specific analysis. Calibration procedures are documented on computer printouts, in the analysis logbook, and/or bench sheets where applicable.

Recalibration is performed at specified time intervals, when indicated by initial or continuing calibration verification procedures, or when required by the contract required method. Calibration procedures are method-specific; consult the appropriate Pace SOP for details regarding initial and continuing calibration.

7. ANALYTICAL PROCEDURES

7.1 PURPOSE AND APPLICABILITY

This section specifies the sources of analytical methods used by Pace-Houston and defines controls on standard operating procedures (SOPs), their content, approval for use, distribution, and revision. A list of preparation and analytical methods performed at Pace-Houston is included as Table 7-1.

7.2 RESPONSIBILITIES

7.2.1 LABORATORY DEPARTMENT MANAGERS

The Laboratory Department Managers shall select laboratory methods and prepare SOPs and any subsequent revisions according to this procedure. SOPs may be authored by a designee, but the Department Managers are ultimately responsible for their preparation and approval.

7.2.2 QUALITY ASSURANCE OFFICER

The Quality Assurance Officer shall review and approve SOPs for use at the laboratory. The QAO is also responsible for the distribution of controlled copies of the SOPs and for maintaining the associated documentation.

7.2.3 LABORATORY GENERAL MANAGER

The Laboratory General Manager shall review and approve SOPs. He/she has overall responsibility for all procedures performed at the laboratory.

7.3 PROCEDURE

7.3.1 METHOD SELECTION

Pace Analytical Services, Inc. will use EPA-approved methodology for the analysis of environmental samples whenever such methods are available. If the applicable agency has not specified an approved method, Pace Analytical Services, Inc. will select a recognized and validated method for use.

While SOPs may vary somewhat from one Pace laboratory to another, all laboratories performing a given analysis will use the same methodology to the extent that the instrumentation and predominant sample matrices at each facility allow.

If a client requests Pace-Houston to use a method developed by the client, the lab will do so, but only for the specified work. Such methods are subject to the controls listed below.

7.3.2 METHOD CONTENT

All analytical procedures will be performed according to a written SOP, incorporating specifics regarding Pace-Houston's quality control procedures, set-up and operation of Pace-Houston's instrumentation, etc. The SOP will address the following:

Purpose - List the property, analyte, or class of compounds measured by the method and summarize the procedure.

Application - Describe the sample matrices, working ranges, and situations to which the procedure applies.

Interferences - Describe those matrix components known to interfere in the analysis and methods for preventing or compensating for an interference when available.

Safety Issues - Describe protective equipment, known safety hazards, and precautions.

Sample Handling and Storage - Describe sample preservation and storage requirements.

Equipment - Describe the instruments, glassware, and other equipment applicable to the procedure.

Reagents - Describe reagents' and standards' concentration, grade, preparation, and use.

Procedure - Describe the sequence of activities to be performed. This should include calibration or standardization, sample pretreatment, sample analysis, calculations, reporting limits, quality control checks,

and special glassware cleaning procedures as appropriate to the method.

References - List the reference method(s) from which information was derived in preparing the method.

7.3.3 SOP REVIEW AND APPROVAL

All SOPs will be approved by the appropriate Laboratory Department Manager, the QA Officer, and the Laboratory General Manager.

7.3.4 SOP DISTRIBUTION

Controlled copies of the appropriate SOPs will be distributed to central files within each laboratory group. Additional controlled copies will be distributed upon request.

7.3.5 SOP REVISION

The first time an SOP is distributed, it is denoted as revision A. Subsequent revisions are denoted as revision B, C, etc.. Revisions must be approved and distributed in the same manner as the original method.

7.4 RECORDS

A revision history of lab SOPs, controlled copy distribution records, and master hard copies of all SOPs will be maintained by the QA Department in support of this procedure.

Table 7-1

Preparation Methods

Test	Water Method(s)	Soil/Waste Method(s)
Toxicity Characteristic Leaching Procedure	—	EPA 1311
Synthetic Precipitation Leaching Procedure	—	EPA 1312
Separatory Funnel Liquid-Liquid Extraction	EPA 3510B	—
Continuous Liquid-Liquid Extraction	EPA 3520B	—
Sonication Extraction	—	EPA 3550A
Waste Dilution		EPA 3580A
Purge and Trap	EPA 5030A	EPA 5030A
Florisil Column Cleanup	EPA 3620A	EPA 3620A
Gel-Permeation Cleanup	EPA 3640A	EPA 3640A
Sulfur Cleanup	EPA 3660A	EPA 3660A
Acid Digestion of Waters for Total Recoverable or Dissolved Metals (FAA/ICP)	EPA 4.1.4, 200.2, 3005A	—
Acid Digestion of Aqueous Samples and Extracts for Total Metals (FAA/ICP)	EPA 3010A	EPA 3010A
Acid Digestion of Aqueous Samples for Total Metals (GFAA)	EPA 4.1.3, 3020A	EPA 3020A
Acid Digestion of Sediments, Sludges, and Soils	—	EPA 3050A
Ammonia Distillation	EPA 350.2	EPA 350.2
Fluoride Distillation	EPA 340.1, SM 4500-F⁻ B	—
Cyanide Extraction	—	EPA 9013

Analytical Methods

Test	Water Method(s)	Soil/Waste Method(s)
Purgeable Halocarbons by GC	EPA 601[1], 8010B[1]	EPA 8010B[1]
Purgeable Aromatics by GC	EPA 602[1], 8020A[1]	EPA 8020A[1]
Phenols by GC	EPA 604[2], 8040A[2]	EPA 8040A[2]
Pesticides/PCBs by GC	EPA 505, 608[1], 8081, CLP SOW OLM01.0-1.8	EPA 8081, CLP SOW OLM01.0-1.8
PCBs by GC	EPA 505, 608[1], 8081	EPA 8081
Herbicides by GC	EPA 515.1, 8151	EPA 8151
Volatile Petroleum Hydrocarbons by GC	EPA 8015A[3]	EPA 8015A[3]
Semivolatile Petroleum Hydrocarbons by GC	EPA 8015A[3]	EPA 8015A[3]
Volatiles by GC/MS	EPA 524.2, 624[1], 8260A, CLP SOW OLM01.0-1.8	EPA 8260A, CLP SOW OLM01.0-1.8

Table 7-1

Analytical Methods (continued)

Test	Water Method(s)	Soil/Waste Method(s)
Base Neutral & Acid Extractables by GC/MS	EPA 625[1], 8270B CLP SOW OLM01.0-1.8	EPA 8270B, CLP SOW OLM01.0-1.8
Metals by ICP	EPA 200.7, 6010A, CLP SOW ILM02.0-2.1	EPA 6010A, CLP SOW ILM02.0-2.1
Metals by Graphite Furnace or Flame AA	EPA 200-Series, 7000-Series, CLP SOW ILM02.0-2.1	EPA 7000-Series, CLP SOW ILM02.0-2.1
Mercury by Cold Vapor AA	EPA 245.1, 7470A, CLP SOW ILM02.0-2.1	EPA 245.5, 7471A, CLP SOW ILM02.0-2.1
Acidity, Total	EPA 305.1, SM 2310	—
Alkalinity, Total	EPA 310.1, SM 2320 B	—
Ammonia	EPA 350.1	EPA 350.1
BOD	EPA 405.1, SM 5210 B	—
CBOD	SM 5210 B	—
Carbon, Total Organic	EPA 415.1, EPA 9060	EPA 9060, ASA 90-3 Walkley-Black[4]
Chloride	EPA 325.2,325.3, 9251, 9252A SM 4500-Cl C	—
Chlorine, Residual	EPA 330.5, SM 4500-Cl G	—
Chromium, Hexavalent	EPA 7196A, SM 3500-Cr D	—
COD	EPA 410.4, HACH 8000	EPA 410.1 Mod.
Color	SM 2120 B	—
Cyanide, Amenable to Chlorination	EPA 335.1, 9010A	—
Cyanide, Weak Acid Dissociable	SM 4500-CN I	—
Cyanide, Total	EPA 335.2, 9010A CLP SOW ILM02.0-2.1	EPA 9010A, CLP SOW ILM02.0-2.1
Cyanide, Reactive	—	EPA 7.3.3
Dissolved Oxygen	EPA 360.1, 360.2,	—
Fluoride, Total	EPA 340.2, SM 4500-F C	EPA 340.2, SM 4500-F C
Iodide	EPA 345.1	—
TOX	EPA 9020B	EPA 9020B
Hardness, Total	EPA 130.2, SM 2340 B	—

Table 7-1

Analytical Methods (continued)

Test	Water Method(s)	Soil/Waste Method(s)
Nitrate, Nitrate+Nitrite	EPA 353.2	—
Nitrite	EPA 354.1	—
Nitrogen, Total Kjeldahl	EPA 351.2	EPA 351.2
Oil and Grease	EPA 413.1, 413.2, 9070, SM 5520 B	EPA 9071A,
Paint Filter Liquids Test	EPA 9095	EPA 9095
Total Petroleum Hydrocarbons	EPA 418.1	EPA 3550A/418.1
pH	EPA 150.1, 9040B	EPA 9045C
Phenolics	EPA 420.1, 420.2	EPA 9066
Phosphorus, Total or Ortho-	EPA 365.2	EPA 365.2
Solids, Total	EPA 160.3, SM 2540 B	SM 2540 G
Solids, Total Dissolved	EPA 160.1, SM 2540 C	—
Solids, Total Suspended	EPA 160.2, SM 2540 D	—
Solids, Total Volatile	EPA 160.4, SM 2540 G	SM 2540 G
Solids, Settleable	EPA 160.5, SM 2540 F	—
Specific Conductance	EPA 120.1, 9050	—
Sulfate	EPA 375.4	EPA 9038
Sulfide, Total	EPA 376.1, SM 4500-S_2^- E	—
Sulfide, Reactive	—	EPA 7.3.4
Sulfite	EPA 377.1	—
Surfactants	EPA 425.1	—
Temperature	EPA 170.1	—
Turbidity	EPA 180.1	—
Waste Corrosivity	—	EPA 1110
Waste Ignitability	—	EPA 1010, 1020A
Fecal Coliform	SM 9222 D	—
Total Coliform	SM 9222 B	—
Heterotrophic Plate Count	SM 9215 B	—

Table 7-1

Analytical Methods
(continued)

Notes:

Methods designated "EPA" are from the following sources:

40 CFR Part 136, Code of Federal Regulations
EPA-600/4-79-20, Methods for Chemical Analysis of Water and Wastes, March 1983 Revision and updates
SW 846, Test Methods for Evaluating Solid Wastes, November 1986, Third Edition and updates
EPA/600/4-91/010, Methods for the Determination of Metals in Environmental Samples, June 1991
EPA/600/4-88/039, Methods for the Determination of Organic Compounds in Drinking Water, December 1988

"CLP SOW" - USEPA Contract Laboratory Program Statements of Work OLM01.1 and ILM02.0

"SM" - American Public Health Association, Standard Methods for the Examination of Water and Wastes, 18th Edition

GC or GC/MS methods modified by the use of capillary columns.

GC method for phenols modified by the use of capillary columns and an ion trap detector.

GC Petroleum Hydrocarbons methods are derived from a modified SW-846 Method 8015A and from American Petroleum Institute Methods "API:AA4, Method for Determination of Gasoline Range Organics, and Q/API:AA5, Method for Determination of Diesel Range Organics.

Methods of Soils Analysis, American Society of Agronomy, 2nd Edition, 1982

8. DATA REDUCTION, VALIDATION AND REPORTING

8.1 PURPOSE AND APPLICABILITY

This section defines the Pace-Houston procedures for data collection, reduction, entry into the LIMS, validation, and reporting. Where procedures for CLP work and non-CLP work diverge, data handling is described for both.

All data is collected, reduced, entered, validated, and reported in accordance with this procedure unless an alternate scheme is outlined in a project-specific plan.

8.2 RESPONSIBILITIES

8.2.1 ANALYSTS

Analysts conduct data collection and reduction in accordance with this procedure.

8.2.2 LABORATORY SUPERVISORS

Laboratory Supervisors review and approve analytical data. This task may be delegated to experienced analysts.

8.2.3 LABORATORY DEPARTMENT MANAGERS

Laboratory Department Managers are responsible for approving sample data and laboratory analysis reports, compiling reports, and authorizing report delivery to the client.

8.2.4 PROJECT MANAGERS

Project Managers prepare cover letters to accompany the report and authorize delivery of the report by the scheduled due date.

8.2.5 QUALITY ASSURANCE DEPARTMENT

For larger or more complex projects, the QA Department may also review laboratory analysis reports and quality control data.

8.3 PROCEDURE

8.3.1 DATA COLLECTION

a. Sample Preparation and Analysis

Sample preparation and analytical activities are documented in sufficient detail to allow the analysis to be recreated. This includes the following, at a minimum. The information must be recorded in a laboratory notebook or on preprinted worksheets, or retrievable from instrument output.

- The analytical activity being performed (i.e., the specific analytical method or preparation method performed).

- The person(s) performing the activity and the date and time that the activity was initiated.

  - When more than one analyst works on an analytical run, each must be identified.

  - If an activity has discrete components that extend over more than one shift, the person performing each component and the date and time that each component is initiated are documented. For example, in suspended solids analysis, filtration of samples and determination of initial weight are performed on one day, and determination of final weight after drying is performed the following day. Thus the analysis breaks down into two discrete components. The analyst performing each component and the date and time that each component is initiated are documented in the analysis log.

- Instrument parameters, including instrument identification and settings. Instrument settings may be referenced to previous documentation of instrument parameters.

- The analytical sequence must be documented (i.e., the chronological order of analysis). The following data for each sample, standard, and QC check run in the analytical sequence must be recorded and/or retrievable from an instrument printout (quantitation report, printer tape, etc.).

Units for all variables are specified, preferably in column headings.

- Pace sample number.
- Client identification if CLP sample.
- QC sample type identification (prep blank, ms, etc.) if QC sample.
- Dilutions made prior to taking a sample aliquot (actual initial and final volumes, not a ratio).
- Sample aliquot/final volume.
- Cell size (colorimetric analyses).
- Instrument reading.
- Final result.
- Percent recovery, RPD, range, or percent difference of quality control checks.

- The calibration curve from which data are quantified, identified by instrument and date run, or by reference to a notebook and page number or a filename, if the initial calibration is not included in the analytical run.
- Identification of the source of standards used for calibration, calibration verification, lab control samples, and matrix spikes, usually by reference to a standards prep notebook and page number.
- Notes regarding any anomalies (e.g., change in color, formation of precipitate) or difficulties (e.g., instrument malfunction) encountered during analysis.
- The notebook identification number on each page.

- For CLP work, data for only one case may be recorded on a page. The sample delivery group is identified at the top of the page.

- Whenever additional pages must be added to a laboratory notebook, the attachment is described on the notebook page and the book and page number are recorded on the attachment. This allows the documents to be re-attached if they become separated.

b. Data Recording and Error Correction

All handwritten data must be recorded using indelible ink. When an error in any hardcopy documentation of data is corrected, the person making the correction draws a single line through the erroneous data so as not to obscure the original entry. He/she then writes his/her initials, the date, and the correct information, if applicable, adjacent to the error. An explanation of the change should also be included, either as a written comment or by using one of the following codes:

E1 - Misspelled or illegible entry
E2 - Mathematical error
E3 - Wrong data entered
E4 - Transposition or sequencing error
E5 - Transcription (copying) error
E6 - Procedural change
E7 - Wrong statement or conclusion
E8 - Unnecessary entry
E9 - Instrument error

8.3.2 DATA REDUCTION

a. Qualitative Identification

Qualitative identification of organic compounds is performed according to CLP Statement of Work guidelines. Second column confirmation by GC is performed upon request or when specified by the requested method.

b. Quantitation

The equations used to calculate final results are specified in the appropriate laboratory methods and SOPs. In general, the following rules concerning reporting limits, significant figures, and rounding rules apply to those calculations.

- Round all calculation results to the correct number of digits as the final calculation step. Do not round any result before reaching the final answer, even in a lengthy calculation.

- To round a number, first determine the number of digits to be reported (the reportable figures). Determine whether the digit to the immediate right of the right-most reportable figure is greater than, equal to, or less than 5. Ignore any digits further to the right unless the number is 5.

- If the number is greater than 5, round up (i,e., increase the right-most reportable figure to the next highest number).

  - If the number is less than 5, simply truncate after the last reportable figure.

  - If the number is equal to 5 and there are non-zero digits to the right of it, round up.

  - If the number is equal to 5 and there are no non-zero digits to the right of it, round up when the preceding figure is odd; truncate when the preceding figure is even.

- Round results at the end of calculations to one or two digits as follows, with the exceptions noted below.

  - If the initial concentration of the sample (i.e., the concentration before any dilutions are taken into account) is less than the reporting limit, express the reporting limit as 1 digit (e.g., <1 mg/L, not <1.0 mg/L).

  - If the initial concentration of the sample is above the reporting limit, and if expressed in scientific notation its exponent would be equal to that of the reporting limit

expressed in scientific notation, report the result to 1 digit. (For example, if the reporting limit is 1 mg/L, the initial concentration is 7.8965 mg/L and no dilutions were made, report the result as 8 mg/L.)

- If the initial concentration is above the reporting limit, and if expressed in scientific notation its exponent would be greater than that of the reporting limit expressed in scientific notation, report the result to 2 digits. (For example, if the reporting limit is 1 mg/L, and the initial concentration is 78.965 mg/L and no dilutions were made, report the result as 79 mg/L.)

Note: (1) For CLP work, report results in accordance with the statement of work, which may differ from these guidelines. (2) For quality control checks and PE samples, express results, recoveries, and relative percent differences using at least three significant figures whenever possible. (Additional reportable figures are not required for method blanks.)

- With some exceptions (organic wastes, low-solids sludges, etc.), solid samples are analyzed for percent moisture and reported on a dry weight basis. The reporting basis for solid samples should always be made clear in the analysis report.

c. Evaluation

The quality control data for each batch or analytical run are evaluated against acceptance limits. (See Section 9, Laboratory Quality Control.) Whenever a quality control result exceeds acceptance limits, with the exception of matrix spike recoveries, corrective action is required prior to turning in data for the batch or analytical run for independent data review. The client must be notified of any QC failure associated with their data and any steps taken to resolve the problem. Corrective actions are documented in the analysis log. When corrective action requires the efforts of someone other than the analyst, or the corrective action will not be completed during the work shift, the analyst completes a nonconformance/corrective action record. (See Section 13, Corrective Action.)

8.3.3 DATA ENTRY

After data reduction, the analyst enters the following data from the analytical run into the laboratory information management system (LIMS).

- Date and time of analysis (time initiated).
- Analyst.
- Instrument.
- Sample results.
- QC sample results.
- Lab notebook reference.

For CLP work, data is entered into the appropriate CLP forms generation software. Quality control data are entered into the LIMS. Sample results are simply entered into the LIMS as "done."

8.3.4 DATA VALIDATION AND REPORTING

The data validation and reporting sequence for CLP and non-CLP work are described below. The independent data and final report reviews conducted by the operations staff are intended to complement one another. The independent data review evaluates the results obtained for many samples for one test; the final report review evaluates the results for all tests run for one sample. Errors and inconsistencies that are not apparent from the initial review may be evident in the second review.

a. Independent Data Review - CLP and Non-CLP Work

- Following data reduction and before or after data entry, the raw data associated with the analytical run - analysis log, instrument output (quantitation reports, chromatograms, spectra, strip chart recordings), calibration curves, etc., are forwarded to the Laboratory Supervisor or his/her designee for <u>independent</u> review and approval. The review encompasses the correctness, acceptability, and completeness of the following elements of data generation and handling. (All elements are not applicable to all tests.)

- Data entry
- Instrument tuning
- Initial calibration
- Continuing calibration/calibration verification
- Calibration blanks
- Method or preparation blanks
- Surrogate and/or lab control sample recovery
- Qualitative identifications
- Quantitation, including units and reportable figures
- Precision of duplicates
- Recovery of matrix spikes
- Holding times
- Data qualifiers/comments

When an unacceptable calibration or quality control check is generated, the data reviewer ensures that appropriate corrective action was taken prior to approving the data. Any defects are corrected. Raw data and data entry are also corrected as necessary. If corrective action cannot be taken, the sample results are qualified appropriately.

- Upon approval of the data, the reviewer initials the lab notebook page(s), worksheet(s), or instrument printout, and indicates approval of the data in the LIMS, which allows the data to proceed to final report generation.

- Following independent data review, preliminary results may be provided to the client when necessary. The results must clearly be

labeled as being preliminary and subject to change upon completion of laboratory review.

b. Report Preparation - Non-CLP Work

- Following independent review, data are available for report preparation through the LIMS. Reports consist of a lab analysis report and a quality control report. The lab analysis report contains the following information:

  - Client name and address (including the person to whose attention the report is being sent).
  - Pace report number.
  - Report date.
  - Pace client number.
  - Pace vendor number (optional).
  - Pace work order number (optional).
  - Project name (optional).
  - Date sampled (when provided to Pace) and date of sample receipt for each sample.
  - Determination, result, and units for each analyte for each sample.
  - Any comments about the sample or results (e.g., presence of a matrix interference).

- If requested by the client, results from organics analyses which fall between the method detection limit and the reporting limit may be reported with a flag indicating that the result is an estimate.

- The quality control report contains the following information as applicable to the analytes:

- Supplemental information, including batch number, method reference, date and time of analysis, analyst, and instrument used for each determination.

- Surrogate standard recoveries.

- Laboratory control sample recoveries.

- Method blank results.

- Matrix spike and duplicate or matrix spike duplicate results.

If any quality control sample result does not meet the applicable acceptance criteria, a footnote or comment will be included with the result in order to explain the nonconformance and corrective action taken, if appropriate.

- The quality control report may be further supplemented with initial and continuing calibration data and/or raw data upon request.

- The report from the LIMS and any supplemental information is forwarded to the Laboratory Department Manager, who compiles and reviews the report, ensuring that all deliverables are included.

c. Final Report Review - Non-CLP Work

When all of the results for the parameters assigned to a sample have passed independent data review, they are evaluated by the Laboratory Department Managers. For some projects, the QA department may also perform a final report review. Errors and inconsistencies that were not evident in the initial review may become apparent when each result is evaluated in light of the results obtained for the other parameters. Specifically, the following are reviewed:

- Units and reportable figures.

- Interparametric relationships (e.g., TDS/conductance, TOC/BOD/COD, dissolved/total, anion-cation balance, where approriate).

- Reasonableness of results given the available information about the sample.

- Method references.

Any problems with the data must be corrected before the final report is approved.

The Project Manager reviews the final report in order to confirm consistency with the client's request for analyses to be performed. The Project Manager also evaluates the data for such findings as historical trends, required reporting limits, permit limits, etc.

d. Report Preparation - CLP Work

When a portion (VOA, BNA, Pesticides/PCBs, Inorganics) of the CLP data package is completed, the Laboratory Supervisor reviews it for technical accuracy and completeness.

Components of the data package are forwarded to the Laboratory Department Managers, who finalize the case narrative, compile the completed data package, and authorize its delivery to the client.

8.4 RECORDS

The following records are maintained in support of this procedure:

8.4.1 HARDCOPY RECORDS

- Analysis logs
- Standard and reagent preparation logs
- Instrument printouts
- Calibration curves
- Complete deliverables for each job, original and any revisions

8.4.2 ELECTRONIC RECORDS

- Records entered at data entry into the LIMS
- Records of data approval in the LIMS

9. LABORATORY QUALITY CONTROL

9.1 PURPOSE AND APPLICABILITY

This procedure provides an overview of the quality control (QC) measures used to assess and control analytical processes at Pace-Houston. Specific information on quality control checks for individual laboratory departments is provided in Pace SOPs for individual analysis methods.

9.2 RESPONSIBILITIES

9.2.1 QUALITY ASSURANCE DEPARTMENT

The Quality Assurance Department (QAD) shall establish and publish acceptance limits for quality control checks and assist laboratory personnel in updating variable limits annually, at a minimum.

9.2.2 LABORATORY ANALYSTS

Laboratory analysts shall compare the results of quality control checks to the published acceptance limits, and shall take appropriate corrective measures whenever acceptance limits are exceeded. Corrective measures shall be documented.

9.3 PROCEDURE

9.3.1 QUALITY CONTROL PROGRAMS

a. Daily Quality Control Program

NOTE: The following discussion of the daily quality control program is general in nature. The test-specific requirements of the methods, as outlined in Pace SOPs, supersede these general requirements. In addition, client- or project-specific QC requirements may supersede those specified in this QA Plan.

- The daily quality control program includes a variety of QC checks inserted into the analysis process by the analysts. These checks include instrument tuning or sensitivity checks, continuing calibration or calibration verification checks, lab control samples, and method blanks. Calibration verification standard, continuing calibration standard, and lab control sample results are calculated as percent recovery. Method blank results are evaluated for the presence/absence of laboratory contaminants. These quality control checks monitor the accuracy of the analytical procedure in the absence of matrix interferences. Decisions to accept or reject analytical results are based on these quality control results.

  Acceptance limits for these checks are taken from EPA methods or are established by Pace-Houston from actual QC data. If these checks fail to meet acceptance limits, corrective action is required prior to continuation of analysis and/or reporting of the data. The corrective action taken for each out-of-control event must be described in the analysis log and approved by the data reviewer. In addition, when the corrective action described in the applicable method is not effective in correcting the problem, or if out-of-control QC data must be reported due to insufficient sample remaining for re-analysis, expired hold time, etc., a nonconformance/corrective action record is completed. (See Section 13, Corrective Action.)

- In addition to these checks, 1 in 10 samples (1 in 20 samples for GC/MS analyses) of a similar matrix is analyzed in duplicate and as a matrix spike, or as duplicate matrix spikes, to evaluate matrix effects. Accuracy is calculated as percent recovery of the matrix spike. Precision is calculated as the relative percent difference (RPD) of duplicates or matrix spike duplicates. Precision is not quantified when one or both results are "less than" values.

  Acceptance limits for these checks are also taken from the EPA methods or are established internally by Pace-Houston. If matrix spike recovery fails to meet acceptance limits and the analytical system yielded acceptable results for calibration standards, lab control standards, and surrogate standards, corrective action is not required. The associated sample

results are qualified, however, to indicate the probable presence of a matrix interference. If precision acceptance criteria are exceeded, reanalysis of the duplicates and all of the positive samples in the batch is required, except in certain cases where the sample matrix may be heterogeneous and the sample aliquot size is small (e.g. TOC or TOX in soil). The corrective action taken is described in the analysis log and approved by the data reviewer. In addition, when the corrective action described in the applicable method is not effective in correcting the problem, or if out-of-control QC data must be reported due to insufficient sample remaining for re-analysis, expired hold time, etc., a nonconformance/corrective action record is completed. (See Section 13, Corrective Action.)

- Control limits for LCS and surrogate recoveries are statistically derived using historical laboratory data; these limits are updated annually, at a a minimum.. In addition to meeting the control limits and QC requirements specified in the method, the statistically-derived control limits are used to monitor performance of the method over time.

b. Performance Evaluation Studies

Pace-Houston participates in a variety of federal and state interlaboratory performance evaluation studies for drinking water, wastewater, and hazardous waste programs. Participation in these programs allows the lab to evaluate its performance against the performance of many other laboratories. Performance evaluation studies are also discussed in Section 10, Performance Evaluations and System Audits.

9.3.2 ACCEPTANCE LIMITS

Acceptance limits for the daily QC program are taken from EPA methods or are established by Pace-Houston from actual QC data as described in this section. Acceptance limits are calculated and summarized annually, at a minimum, and distributed to laboratory operations personnel by the QAD.

a. Fixed Limits

In general, acceptance limits for GC, GC/MS, and metals analyses for tuning, initial and continuing calibration, method blanks, and precision and accuracy of matrix spikes and duplicates or duplicate matrix spikes are based on acceptance limits established in EPA methods.

b. Variable Limits

Variable limits are based on laboratory-generated data and are updated annually, at a minimum.

- Accuracy

  Acceptance limits for percent recovery of lab control samples and GC and GC/MS surrogate standards are calculated from actual QC data. The mean (x) and standard deviation (s) are calculated from the most recently generated percent recovery data. A minimum of 20 values are necessary to establish limits; up to 100 values will be used when available. Outliers, which are excluded from the calculation of acceptance limits, are identified as described in paragraph 9.3.5.

  If the data generated are insufficient to calculate acceptance limits, and the method does not provide acceptance criteria, the following limits will apply:

  - Inorganic chemistry: 75.0 - 125% recovery
  - Metals: 75.0 - 125% recovery (water); 50.0 - 150% recovery (soils)
  - Organic chemistry - Volatiles: 75.0 - 125% recovery
  - Organic chemistry - Base-neutrals and other extractables: 50.0 - 150% recovery
  - Organic chemistry - Acids: 25.0 - 125% recovery.
  - Other analyses: 75.0 - 125% recovery

Acceptance limits are calculated as follows, where x_i represents the individual values and n is the number of values:

Parameter	Symbol	Formula
Upper Control Limit	UCL	$\bar{x} + 3s$
Upper Warning Limit	UWL	$\bar{x} + 2s$
Center Line (mean)	$\bar{x}$	$(\Sigma x_i)/n$
Lower Warning Limit	LWL	$\bar{x} - 2s$
Lower Control Limit	LCL	$\bar{x} - 3s$

- Precision

  Acceptable relative percent difference (RPD) of duplicate analyses is ≤ 20% for duplicate results greater than 10 times the method detection limit (MDL). When one or both results are ≤10 times the MDL, the RPD acceptance range is ≤ 67%. These limits are not applicable to cases where the sample matrix may be heterogeneous and the sample aliquot size is small (e.g. TOC or TOX in soil).

- Acceptance Limit Updates

  Acceptance limits will be updated annually at a minimum, when 20 or more new values have been generated. The summary of acceptance limits is revised and distributed to the appropriate lab groups after each update.

9.3.3 CONTROL CHARTS

In order to monitor each analysis for trends, laboratory control sample (LCS) recoveries are plotted on control charts (see Figure 9-1). Separate control charts are maintained for LCSs prepared in aqueous and solid matrices, where applicable. The LCS is the best indicator of a problem in the preparation step of many analyses. On tests which do not involve a distinct preparation step, as in volatile organics and several wet chemistry tests, an independent initial calibration verification (ICV) standard and/or continuing

calibration verification (CCV) standard from a second source is used to verify instrument and analyst performance, as well as initial calibration. This ICV or CCV is also designated an LCS for QC data reporting purposes.

9.3.4 OUT-OF-CONTROL SITUATIONS

Whenever an out-of-control situation occurs, with the exception of matrix spike recoveries (see 9.3.1.a.), corrective action is required prior to continuation of analysis and/or reporting of the data for the entire batch. The corrective action taken for each out of control event must be described in the analysis log. In addition, if out-of-control QC data must be reported due to insufficient sample remaining for re-analysis, expired hold time, etc., a nonconformance/corrective action record is completed. (See Section 13, Corrective Action.)

a. Fixed Limits

Analyses are out of control whenever the acceptance limits are exceeded.

b. Variable Limits

Analyses are out of control whenever the acceptance limits are exceeded. In addition, any of the following situations occurring on LCS control charts must be reported to the QAD. After evaluating the data, the QA Officer, along with the Laboratory Department Manager or Supervisor, will determine the required corrective action.

- 2 consecutive points are outside the warning limits
- 7 consecutive points are on one side of the center line
- 7 consecutive points increase or decrease
- An obvious cyclical pattern is observed in the distribution of points

9.3.5 IDENTIFICATION OF OUTLIERS

Outliers, which are excluded from the data used to calculate acceptance limits, are identified as follows (according to the procedure described in

ASTM E178-80, Sections 4.1 and 4.2):

- $\bar{x}$, s, and n are those values calculated from the current set of data.
- x_f is that value in the current set of data furthest from $\bar{x}$.
- $T_{1\%}$ is the critical value for T at the upper 1% significance level, corresponding to n, from Table I in ASTM E178-80.
- If the absolute value of $(\bar{x} - x_f)/s \leq T_{1\%}$, x_f is not an outlier. Use this value and all other values in the data set to calculate acceptance limits.
- If the absolute value of $(\bar{x} - x_f)/s > T_{1\%}$, x_f is an outlier. Delete this value from the data set and do not use it to update acceptance limits. Repeat the test for outliers, using the new x, s, n, and x_f from the current data set, until no outliers are identified. More values from historical data may be added to the data set if n becomes less than 20.

9.3.6 METHOD DETECTION LIMITS

Method detection limits (MDLs) are determined for each analyte on each instrument by performing MDL studies as specified in 40 CFR Part 134, Appendix B, *Definition and Procedure for the Determination of the Method Detection Limit*, Revision 1.11. MDLs are updated annually, at a minimum.

9.3.7 REPORTING LIMITS / PRACTICAL QUANTITATION LIMITS

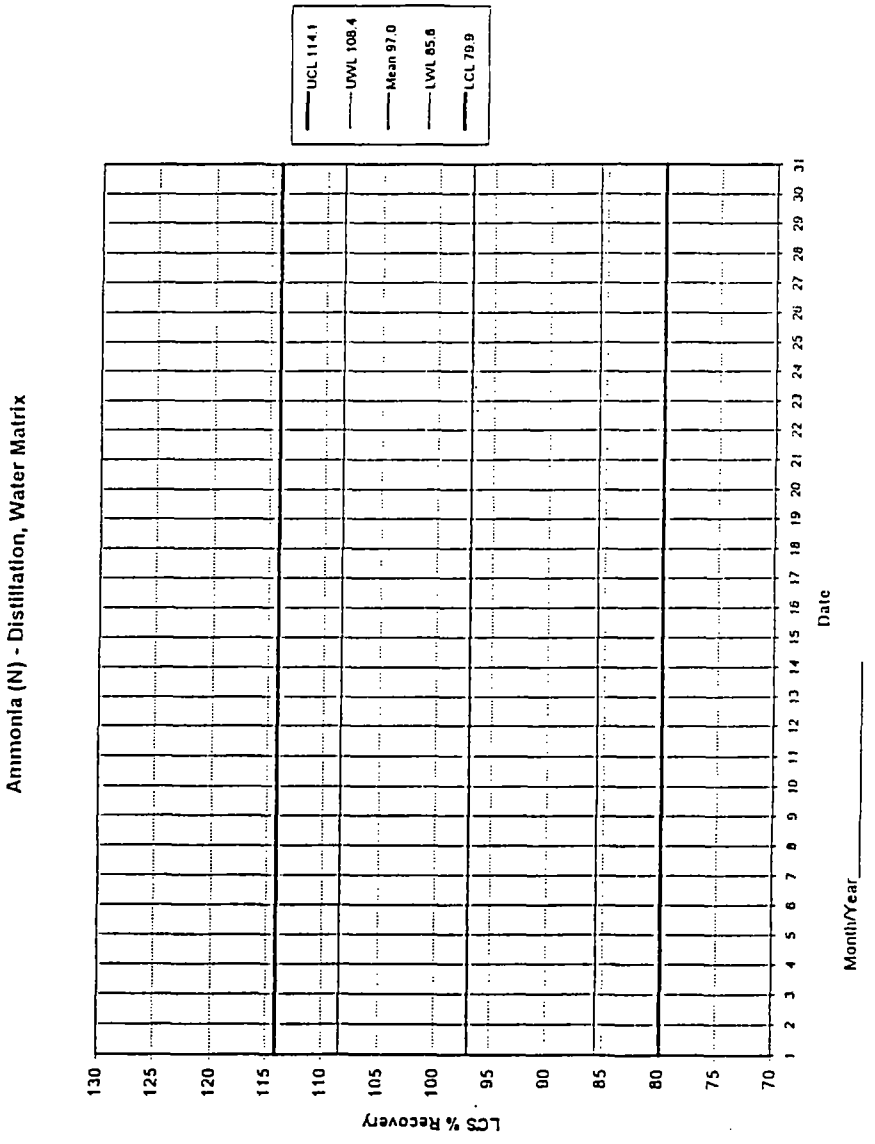
The reporting limit, or practical quantitation limit (PQL), for a given parameter is a nominally chosen value which can routinely be detected and reported as greater than zero in the majority of sample matrices encountered in the laboratory. Reporting limits are always greater than the corresponding MDLs and are established based upon the noise level of the instrumentation, experience in performing the analysis, and typical reporting limits required by regulatory agencies and clients. A reporting limit for a given parameter may vary according to the needs of the client.

9.4 RECORDS

All quality control data and a history of acceptance limits will be maintained by the Quality Assurance Department in support of this procedure.

Figure 9-1

LCS Control Chart



10. PERFORMANCE EVALUATIONS AND SYSTEM AUDITS

10.1 INTERNAL AUDITS

The records, systems, and procedures of each laboratory department are audited annually, at a minimum, by the Quality Assurance Department. The data is reviewed for completeness, accuracy, and adherence to standard operating procedures. Random project files are evaluated for compliance to procedures throughout the analytical process (i.e., from sample receipt through the final report). Department Managers and Supervisors check all logbooks and records to ensure appropriate documentation of analyses are being recorded in the proper manner.

10.2 EXTERNAL AUDITS

Pace-Houston is audited as required by regulatory agencies to maintain laboratory certifications and approvals. Commercial clients with laboratory auditing programs typically conduct on-site audits at least once per year, and perform data audits on a project-specific basis. These audits are conducted by the client or a consulting firm specializing in this service and operating under contract to the client.

10.3 PERFORMANCE EVALUATIONS

Pace-Houston participates in the US EPA semi-annual drinking water (WS Series) and semi-annual wastewater (WP Series) Performance Evaluation Studies (four studies per year). The laboratory also participates in various client-sponsored performance evaluations by analyzing QC samples prepared and submitted by commercial clients in conjunction with their own QA program. In addition, the Pace-Houston Quality Assurance Department periodically submits to the laboratory single-blind QC check samples, in order to internally monitor performance of parameters which are not evaluated by external PE programs.

11. PREVENTIVE MAINTENANCE

Pace-Houston employs a full-time instrument specialist to perform maintenance and repairs of most analytical instruments. Maintenance and repair of some instruments, such as analytical balances, is performed under service contracts with outside vendors. A list of major instruments is included as Table 11-1.

All instruments and equipment receive routine preventive maintenance, which is recorded in instrument specific maintenance logs. Routine maintenance ensures that the equipment is operating under optimum conditions, reducing the possibility of instrument malfunction.

Preventative maintenance procedures including lubrication, source cleaning, detector cleaning, and the frequency of such maintenance are performed according to the procedures recommended in the manufacturer's instrument user manual.

Chromatographic carrier gas purification traps, injector liners, and injector septa are cleaned or replaced on a regular basis. Precision and accuracy data are examined for trends and excursions beyond control limits to determine evidence of instrument malfunction. Maintenance must be performed when the instrument begins to degrade as evidenced by the degradation of peak resolution, shift in calibration curves, decreased sensitivity, or failure to meet one or another of the quality control criteria. Instrument logbooks containing maintenance and repair records are kept in the laboratories at all times. The laboratories also maintain adequate supplies of spare parts such as GC columns, syringes, septa, injection port liners, and electronic parts to minimize potential down-time.

In the event of equipment malfunction that cannot be readily resolved by laboratory personnel, service is obtained from the instrument vendor or manufacturer. Should instrument failure preclude completion of analyses within contract requirements (i.e., holding times), Pace-Houston will contact the client to determine alternative strategies, including use of another Pace Analytical Services laboratory.

Table 11-1

Pace-Houston Laboratory Major Instruments

Type		Make & Model	Year of Purchase
GC/MS	(3)	Finnigan INCOS 50	1986, 1987, 1987
GC/MS	(2)	Finnigan INCOS 500	1990, 1992
GC/MS		Finnigan 5100	1990
GC/MS	(2)	Finnigan 4500	1986, 1990
GC/MS	(2)	Hewlett Packard 5972	1994, 1994
GC/MS		Hewlett Packard 5971A	1995
GC w/ECD	(3)	Varian 3400	1987, 1987, 1991
GC w/ECD		Hewlett Packard 5890-II	1990
GC w/dual ECD	(2)	Hewlett Packard 5880A	1984, 1984
GC w/FID		Varian 3400	1989
GC w/FID		Hewlett Packard 5890	1980
GC w/PID	(2)	Hewlett Packard 5890-II	1991, 1991
GC w/PID	(2)	Varian 3300	1987, 1987
GC w/Ion Trap		Finnigan Magnum	1993
GPC Unit		ABC Labs 1002B	1988
ICP Spectrophotometer		Perkin-Elmer P1000	1991
ICP Spectrophotometer		Perkin-Elmer P40	1989
ICP Spectrophotometer		Thermo-Jarrell Ash 61E	1993
ICP Spectrophotometer		Thermo-Jarrell Ash 61E Super Trace	1994
Graphite Furnace AA Spect.		Perkin-Elmer 3030	1987
Graphite Furnace AA Spect.		Perkin-Elmer 5100	1991
Graphite Furnace AA Spect.		Perkin-Elmer 5100P	1994
Graphite Furnace AA Spect.		Perkin-Elmer 4100ZL	1990
Flame AA Spectrophotometer		Perkin-Elmer 3030	1986
CVAA Mercury Analyzer		Perkin-Elmer FIMS	1994
CVAA Mercury Analyzer		Bacharach 50B	1993
Autoanalyzer	(2)	Alpkem RFA300	1988, 1993
Autoanalyzer		Bran & Lubbee TRAACS-800	1988
TOC Analyzer		Dohrmann DC-80	1987
TOC Analyzer		Shimadzu ASI 5000 S	1991

Table 11-1
(continued)
Pace-Houston Laboratory Major Instruments

Type		Make & Model	Year of Purchase
TOX Analyzer		Mitsubishi TOX-10 Sigma	1995
TOX Analyzer		Dohrmann DX20	1986
TOX Analyzer		Mitsubishi TOX-10+	1988
IR Spectrophotometer		Perkin-Elmer 1310	1989
UV-Vis Spectrophotometer		Milton Roy 301	1988
UV-Vis Spectrophotometer	(2)	Milton Roy 401	1992, 1994

12. ASSESSMENT OF PRECISION, ACCURACY, COMPLETENESS, REPRESENTATIVENESS, AND COMPARABILITY

12.1 ACCURACY

Accuracy is indicated by the measure of the difference between observed and true values. A minimum of one of every 20 environmental samples for organic analyses or one in 10 for inorganic analyses is spiked with a standard solution to assist in evaluating the accuracy of the method for a given sample matrix through calculation of percent recovery of the matrix spike.

Each batch of up to 20 samples is prepared with a laboratory control sample (LCS) to ensure the analysis system is operating in control. The percent recovery for the LCS is calculated by comparison of the value obtained for the analysis with the true value for the LCS.

Surrogate compounds are spiked into samples analyzed by GC and GC/MS methods. The percent recoveries of the surrogates are used as an indicator of the accuracy of the analysis.

The calculation of percent recovery is performed in the following manner:

- Matrix Spike Recovery -

$$\% \text{ Recovery} = \frac{SSR - USR}{SA} \times 100\%$$

where:
SSR = Spiked sample result
USR = Unspiked sample result
SA = Spike added

- Surrogate or Lab Control Sample Recovery -

$$\% \text{ Recovery} = \frac{\text{Result obtained}}{\text{True value}} \times 100\%$$

See Section 9, Laboratory Quality Control, for a discussion of control limits and corrective action for out-of-control events.

12.2 PRECISION

Precision refers to the reproducibility of results obtained for the analyses of duplicate samples or matrix spiked duplicate samples. One out of every 20 samples of similar matrix analyzed by each method for organics (1 in 10 for inorganics) is run in duplicate or as matrix spike duplicates for determining precision.

The results of the duplicate analyses are computed and the absolute relative percent difference (RPD) is calculated as follows:

$$RPD = \frac{(R1 - R2)}{\frac{1}{2}(R1 + R2)} \times 100\%$$

where: R1 = First replicate result
R2 = Second replicate result

The RPD must fall within set acceptance limits for the results to be accepted and subsequent data validated. See Section 9, Laboratory Quality Control, for a discussion of control limits and corrective action for out-of-control events.

12.3 COMPLETENESS

Data completeness can be quantified during data assessment. A statement of expected completeness for a project is one data quality objective. Pace-Houston has established the ability to provide data, meeting QC acceptance criteria, for 95% or more of the requested determinations. It is incumbent for planners to identify any sample types, such as control or background locations, which require 100% completeness.

12.4 REPRESENTATIVENESS

Representativeness is a qualitative element that is related to the ability to collect a sample that reflects the characteristics of that part of the environment that is to be assessed. Sample representativeness is dependent on the sampling techniques used and is considered individually for each project. It is specifically addressed in each work plan. The laboratory recognizes its role in achieving within-sample representativeness and uses appropriate techniques to obtain a representative aliquot. Some test are performed in quadruplicate if obtaining a representative aliquot is precluded by sample heterogeneity and small aliquot size.

12.5 COMPARABILITY

The objective of comparability is to produce results that do not differ significantly from those produced by other parties for the same purpose. Pace-Houston uses SOPs based on EPA-approved methods in order to achieve comparability with data from previous studies and from other laboratories. SOPs are written to incorporate the method requirements specified by the Pace corporate office in minimum requirements documents (MRDs), thus promoting comparability within the Pace network of laboratories. Pace-Houston participates in external and inter-laboratory performance evaluation (PE) studies as an additional means of establishing comparability in the laboratory.

13. CORRECTIVE ACTION

For purposes of the Pace-Houston corrective action system, nonconformances are defined as:

- Deviations from methods, SOPs, client requirements, internal QA/QC requirements, or good lab practices, which may have an effect on data or the client's interpretation of data, or

- Potential quality problems identified by PE samples, external clients or agencies, or Pace-Houston employees.

- Complaints, defined as expressed dissatisfaction with data or procedures related to data quality, from clients or other parties.

In order to identify, track, and prevent the recurrence of problems, nonconformances and the corrective actions taken are documented on a corrective action record (see Figure 13-1).

The steps that may comprise a closed-loop corrective action system are as follows:

1. Define the problem.

2. Assign responsibilities for problem investigation.

3. Communicate the problem to affected manager(s) and project management, where applicable.

4. Investigate and determine the cause of the problem (check all calculations, re-analyze the sample, verify the integrity of the spiking solution, laboratory control sample, or calibration standard, check instrument and operating conditions to preclude the possibility of malfunctions or operator error, etc.).

5. Determine the corrective action(s) necessary to eliminate the problem and to prevent its recurrence.

6. Assign and accept responsibilities for implementing the corrective action.

7. Report the nonconformance and corrective action taken to the Quality Assurance Department.

8. The completed corrective action record is closed by the QA Department and copies routed to the originator, the client file, and the Laboratory General Manger.

If investigation of a complaint reveals a systematic nonconformance to the QA program, an internal audit will be conducted by the QA Department to determine the scope of the problem, any affected data, and corrective action needed to prevent recurrence. If, as a result of the audit, a client's data are shown to be incorrect, the client will be immediately notified in writing and a corrected report delivered, when appropriate.

Figure 13-1

Nonconformance/Corrective Action Record

95-0-

Pace Analytical Services, Inc. - Houston Laboratory
NONCONFORMANCE / CORRECTIVE ACTION RECORD
See instructions on reverse side.

Originator: _____ Date: _____
Client: _____ Affected sample nos.: _____
Test: _____ Book & page no.: _____

Sample Integrity	Sample Analysis	External Origin
Route to PM, contact client ASAP	Take corrective action in lab, comment on final report	Take corrective action in lab, reissue final report when appropriate
__Preservative __Other __Temperature __VOA headspace __Container __ID/labeling __Holding time __Sampling	__LCS recovery __Other __Blank contamination __Calibration __Compound ID, qualitative __Calculation/quantitation __SOP/method deviation	__PE results __Other __Client problem/request __Agency requirement

Nonconforming condition: _____

ROUTE TO: _____ COPY TO: _____ _____
Responsible individual Affected manager Project manager

Corrective action (temporary fix): _____

By: _____ Date completed: _____

Preventive action (permanent fix): _____

By: _____ Date completed: _____

ROUTE ORIGINAL TO QA DEPARTMENT

Additional comments: _____

Closed by: _____ Date: _____

COPY TO ORIGINATOR, CLIENT FILE, AND GENERAL MANAGER

14. QUALITY ASSURANCE REPORTS TO MANAGEMENT

14.1 OBJECTIVE

This section describes the methods used by Pace-Houston to ensure that management personnel are informed of situations which could affect the performance of the laboratory.

14.2 PROCEDURE

Quarterly reports are provided by the Quality Assurance Officer to the Corporate Director of Quality and the Laboratory General Manager. This report addresses the quarterly quality assurance activities including details of corrective actions implemented, audit results, performance evaluation results, and other major quality issues when they arise.

In addition to the quarterly QA reports, weekly meetings are used to communicate to the laboratory's management staff pertinent information related to QA/QC issues.

15. TRAINING

15.1 INTRODUCTION

This section of the QA Plan describes the Pace-Houston program for training in areas where quality is affected. Specific areas where training must be documented include:

- Analytical methods training
- Quality assurance/quality control (QA/QC) training
- Safety training

Other types of training also occur but are not at this time required to meet the requirements of the quality assurance program; these include such subjects as computer training, continuing education, seminars, and total quality management (TQM) training.

Specific details of the training program at Pace-Houston can be found in Pace SOP number HO-P-004, *Training Procedures*.

15.2 ANALYTICAL METHODS TRAINING

All analysts are trained and supervised in performing specific analytical procedures before working unsupervised. The Laboratory Department Managers are responsible for training within their work groups. A supervisor or senior analyst typically conducts the training, using method-specific analytical SOPs as training guides.

A training record is used to document the trainee's proficiency in performing the procedure. For some methods, analyst proficiency is also demonstrated through the analysis of standard materials, with documentation retrievable from the lab notebook and raw data.

Each Department Manager will determine the frequency of retraining, based on revisions to the SOPs or the methods themselves.

15.3 QA/QC TRAINING

The Quality Assurance Officer (QAO) conducts training of new hires in general QA/QC principles. The QAO determines the frequency of retraining, based on deficiencies determined during performance evaluation or systems audits. Additionally, the QAO and/or Project Manager may provide project-specific training before the laboratory analyzes samples for a major project or a project with specific QA/QC or analytical requirements.

A training record is used to document each trainee's attendance at a given training session.

15.4 SAFETY TRAINING

The laboratory Safety Officer conducts training of new hires in the Pace safety program and Chemical Hygiene Plan, and in hazard communications (HAZCOM). Annually all employees are given safety training, which includes the following subjects:

- Safety and Chemical Hygiene Plan
- HAZCOM
- Blood-borne pathogens
- Fire safety

In addition, selected employees are trained annually in respirator use, waste handling/hazardous materials (HAZMAT), and/or first aid and CPR. The Safety Officer also conducts other safety-related training as needs arise. A training record is used to document each trainee's attendance at a given training session.

15.5 TRAINING RECORDS

Records are maintained documenting each employee's training in analytical methods, QA/QC principles, and safety. Training records shall specify the trainee, trainer, date, and subject of the training session. The results of proficiency testing, where applicable, should also be included.

16. PROCUREMENT AND CONTROL OF MATERIALS AND SERVICES

16.1 INTRODUCTION

This section of the QA Plan describes the policies and procedures for the control of purchased materials and services which affect quality. The procurement of materials and services must be preceded by a planning phase, in which the requirements of specific EPA methods, projects, or contracts are evaluated. This includes defining the acceptance criteria for standards, reagents, glassware, instrumentation, and subcontracted laboratory services. Detailed procedures for the procurement of materials and services are found in Pace SOP number HO-P-005, *Control of Purchased Items and Services.*

16.2 LABORATORY MATERIALS

16.2.1 PROCUREMENT

In planning for procurement of materials, acceptance criteria must be defined before selection of a supplier. The supplier should be provide evidence that the materials meet the acceptance criteria before being put into use. General guidelines for environmental laboratory materials include the following:

- Standards - calibration standards should be NIST-traceable, if available. Use a second source (manufacturer different from calibration standards) for calibration verification standards.

- Reagents and chemicals - use grade specified in method (i.e., reagent grade conc. HCl, purge and trap grade methanol).

- Volumetric glassware - use "Class A" only.

- Weights used to verify balance calibration - use "Class S" only. Certificates of calibration should be supplied.

- Instrumentation - use equipment described in the method, with adequate sensitivity, working range, and reliability. Certificates of calibration should be supplied for such items as millivolt standards

and NIST-traceable thermometers, where the item will be used to calibrate other equipment in the laboratory.

16.2.2 MATERIALS CONTROL

In order to ensure that deteriorated reagents and chemicals are not used, a label is affixed to each container when received at the laboratory, prompting for date received, date opened, and expiration date. Receiving personnel complete the blank for date received; when first opening the container, the analyst completes the label by supplying the date opened and expiration date. If the manufacturer has not specified an expiration date, the analyst completes the blank with "None".

Solvents used for organic extractions are prescreened for contamination by the laboratory whenever a new lot is received. If analysis of the solvent reveals a contaminant, the lot is rejected. If the solvent contains no detectable contaminants, the lot may be reserved by the supplier in large quantities for use by Pace-Houston. In addition, preservatives used in sample containers are prescreened whenever a new lot is received.

Reagents and chemicals are stored in appropriate containers, with incompatible materials segregated (see the Pace Analytical Services, Inc. Chemical Hygiene Plan). Acids are stored with the containers in separate plastic trays. Solvents are stored in designated solvent cabinets. Standards and working reagents are stored in refrigerators maintained at 2-6° C or in freezers, where appropriate.

Preparation of reagents and standards (calibration, calibration verification, surrogate spike, and matrix spike) is documented in support of sample analysis in a lab notebook as follows:

- Compound or element name and/or formula and final concentration or normality.

- Identification number, which takes the following form:

  999-99-888-7

  where "999-99" and "888" are the notebook number and page number of the entry, respectively, and "7" is the number of the entry on the standards notebook page.

- Manufacturer and lot number of all standard materials.
- Date prepared and preparer.
- Expiration date.
- Brief description of preparation. This may be referenced from a previous description of preparation or the lab method, providing that the standard or reagent was prepared in exactly the same fashion as the referenced description.

Each newly-received lot of calibration standards must be verified against the standard currently in use before being used for calibration in the laboratory. Procedures and criteria for standard verification are found in Pace SOP number HO-P-009, *Standard Verification*.

Bottles or flasks containing standards or reagents must be labeled with the following:

- Compound or element name and/or formula, and final concentration or normality.
- Identification number.
- Lot number
- Date prepared and preparer.
- Expiration date.

16.3 LABORATORY SERVICES

With prior consent by the client, Pace-Houston may use other laboratories in the Pace network to perform analyses not within Pace-Houston's capabilities or capacity. Subcontracted laboratory services (i.e., services of non-Pace laboratories) are also occasionally used by Pace-Houston with the client's consent.

When procuring subcontracted laboratory services, the minimum criteria to be met by the subcontracted laboratory must be established. The following should be addressed, at a minimum:

- Methods to be performed
- State or federal certifications or approvals required
- Special quality control requirements specified by project
- Report deliverables required
- Financial responsibility and insurance
- Contractual flowdowns
- Client's consent - blanket, or case-specific

Once a potential candidate lab is selected, the lab's quality assurance plan is reviewed by the Pace Quality Assurance Officer (QAO). A laboratory may not be used for subcontracted analyses without prior approval by the QAO. If the QA Plan is not available or appears inadequate, the QAO may schedule an audit of the candidate laboratory's facility.

In order to monitor the subcontracted laboratory's performance on an ongoing basis, the QAO shall periodically review subcontractors' analysis results and QC data.

STANDARD OPERATING PROCEDURE

PREPARATION OF SOLID SAMPLES FOR TOTAL SULFIDE

SOP Number:	**HO-I-061-A**
Author:	**Gene Schwab**
Effective Date:	**June 20, 1996**
Supercedes:	**First Issue**

Approvals:

General Chemistry Supervisor — **Date** 6/28/96

Inorganic Laboratory Manager — FOR RUSSELL MORGAN — **Date** 6-28-96

Quality Assurance Officer — **Date** 6-28-96

CONTROLLED COPY
RCRA / WASTE 603

I. PURPOSE

This method is used for the determination of total sulfide released from soils, sediments, and solid wastes.

II. SCOPE AND APPLICATION

A. This method is applicable to all soils and solid wastes, with the condition that samples which are combined with acids do not form explosive mixtures.

B. This test measures only the evolved hydrogen sulfide at the test conditions. It is not intended to measure forms of sulfide other than those that are evolvable under the test conditons.

III. SAFETY INFORMATION

A. Wear lab coat and safety glasses with side shields at all times while performing this procedure. Wear gloves to avoid skin contact with the samples and reagents.

1. Should skin or eye contact occur, flush the exposed area(s) with large amounts of water and seek immediate medical attention.

2. Never pipet materials by mouth. Use a rubber bulb or other approved suction device to transfer materials by pipet.

B. Handle and store all reagents in accordance with the precautions listed on the material safety data sheets (MSDS's).

1. Consult the MSDS for each reagent listed in this procedure before use. The MSDS will provide pertinent information on toxicity, safety precautions and storage conditions.

2. Always consult the label on the reagent bottle for up-to-date information on safety precautions during handling, preferred storage conditons, and expiration date.

3. Label all flasks, vials, etc. with the intended contents prior to filling. Follow established laboratory procedure in completing and affixing labeling information to equipment.

C. Handle all glass equipment with care, particularly during periods of heating and cooling.

IV. RESPONSIBILITIES

A. ANALYSTS

1. All analysts are responsible for adherence to this SOP.

2. All analysts are responsible for notifying the section Supervisor/ Manager of any required revisions to this SOP.

B. DEPARTMENT SUPERVISOR/MANAGER

1. The Department Supervisor/Manager is responsible for ensuring adherence to this SOP.

2. The Department Supervisor/Manager is responsible for performing an annual review of this SOP.

C. QUALITY ASSURANCE OFFICER

1. The QAO is responsible for conducting periodic laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Regional Management and Corporate Quality.

2. The QAO is responsible for determining distribution of and maintaining document control of this SOP.

IV. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. Required revisions will be incorporated at the time of the review.

C. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

V. DISTRIBUTION

Distribution of this SOP will be determined by the QAO.

VI. SUMMARY OF METHOD

An aliquot of the soil or waste is acidified in a closed system. The hydrogen sulfide gas generated is purged by nitrogen into a scrubber containing zinc acetate, where zinc sulfide is precipitated. The scrubber solution is then analyzed according to Pace SOP # HO-I-016, *Sulfide - Titrimetric*.

VII. SAMPLE HANDLING AND PRESERVATION

A. Samples containing, or suspected of containing, sulfide wastes should be collected with a miminum of aeration. The sample bottle should be filled completely, excluding all head space, and stoppered. Analysis should commence as soon as possible, and samples should be kept refrigerated and stored in the dark until analysis begins.

B. Testing will be performed in a ventilated hood.

VIII. APPARATUS

A. Round-bottom flask: 1000-ml with a two-hole stopper, fitted with a fritted gas-diffusion tube and a gas outlet tube.

B. Stirring apparatus: To achieve approximately 30 rpm. This may be either a rotating magnet and stirring bar combination or an overhead motordriven propeller stirrer.

C. Flexible tubing: For connection from nitrogen supply to apparatus.

D. Nitrogen gas: With two-stage regulator.

E. Absorption flasks: 500 ml capacity flasks with glass tube and air stone, and an air outlet tube.

IX. REAGENTS

A. Zinc acetate solution, 2N: Dissolve 220 g $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in 870 ml reagent water; this makes 1 liter of solution.

B. Sulfuric acid, conc. reagent grade.

X. PROCEDURE

A. Measure 5 ml zinc acetate solution and 495 ml distilled water into the absorption flask.

B. Assemble the system and adjust the flow rate of nitrogen, using the regulator. Flow should be 60 mL/Min. Purge the system for 2 minutes.

C. Add to the system 10.0 g of the waste to be tested. Record weight on the raw data sheet. Add 500 ml of distilled water to the reaction flask.

D. With the nitrogen flowing, acidify the sample in the reaction flask with 10 ml conc. H_2SO_4 and immediately replace the prepared 2-hole stopper tightly. Begin stirring the sample in the reaction flask.

E. After 60 minutes, close off the nitrogen and disconnect the scrubber. Transfer the solution in the scrubber to a plastic screw-top bottle and proceed to Pace SOP # HO-I-016 to determine the amount of sulfide in the sample.

XI. QUALITY CONTROL

A. Prepare a method blank for every batch of up to 20 samples. If the method blank result is not less than the reporting limit, re-prep a new method blank and all samples in the batch with positive hits.

B. Prepare a laboratory control sample (LCS) for every batch of up to 20 samples. If the LCS recovery does not fall within statistical control limits, re-prep a new LCS and all samples in the batch.

C. Prepare a matrix spiked sample for every batch of up to 20 samples. If recovery is not within the control limits established for the LCS, and the LCS recovery is acceptable, flag the data as indicative of possible matrix interference.

XII. REFERENCE

EPA SW-846, *Test Methods for Evaluating Solid Waste*, Method 9030.

STANDARD OPERATING PROCEDURE

Gasoline Range Organics

SOP NUMBER: HO-0-030

AUTHOR: Matt Hearne

EFFECTIVE DATE: January 23, 1997

APPROVAL

Laboratory Operations Manager	Date
Quality Assurance Officer	1/23/97 Date

METHOD FOR DETERMINATION OF GASOLINE RANGE ORGANICS

1. Scope and Application

1.1 This method is used o determine the concentration of gasoline range organics in water and soil. This corresponds to an alkane range of C_6 - C_{10} and a boiling point range between approximately 60°C and 170°C. Gasoline or other specific petroleum products may be identified by the use of pattern recognition.

1.2 The practical quantitation limit (PQL) of this method for gasoline range organics is approximately 5 mg/kg for soils and 0.1 mg/L for ground water.

1.3 This method is based on a purge-and-trap, Gas Chromatography (GC) procedure. This method should be used by, or under supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs. The analyst should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.4 With the optional PID detector, this method can be extended for the specific determination of volatile aromatics (BTEX) as specified in SW-846 Method 8020.

1. Summary of Method

2.1 This method provides gas chromatographic conditions for the detection of certain volatile petroleum fractions such as gasoline. Samples are analyzed utilizing purge-and-trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a flame ionization detector (FID) or FID with photoionization detector (PID) in series (PID first in the series). Quantification is based on FID detector response to a gasoline component standard.

2.2 This method is suitable for the analysis of waters, soils or wastes. Water or low level soil samples can be analyzed directly for gasoline range organics by purge-and-trap extraction and gas chromatography. High level soil or waste samples are dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is analyzed by purge-and-trap GC following the normal water method.

3. Definitions

3.1 Gasoline Range Organics (GRO): All chromatographic peaks eluting between 2-methyl pentane and 1,2,4-trimethylbenzene. Quantification is based on a direct comparison of the area within this range to the total area of the 10 components in the gasoline component standard.

3.2 Gasoline Component Standard: A ten component blend of typical gasoline compounds (Table 3). This standard serves as a quantification standard and a retention time window-defining mix for gasoline range organics. It may also be used as the PID calibration standard for the optional determination of BTEX by Method 8020.

3.3 Gasoline Control Standard: A commercial gasoline used by the laboratory as a quality control check. See 7.2.

3.4 Surrogate Control Sample: A reagent water or method blank sample spiked with the surrogate compounds used in the method. The surrogate recovery is used to evaluate method control. See 7.8.

3.5 Laboratory Control Sample: A reagent water or method blank sample spiked with the gasoline control standard. The spike recovery is used to evaluate method control and must be greater than 50%.

3.6 Other terms are as defined in SW-846.

4. Interferences

4.1 High levels of heavier petroleum products, such as diesel fuel, may contain some volatile components producing a response within the retention time range for gasoline. Other organic compounds, including chlorinated solvents, ketones and ethers are measurable. As defined in the method, the GRO results include these compounds.

4.2 Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. A trip blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe and/or purging device must be rinsed between samples with reagent water or solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank of reagent water to check for cross contamination. For volatile samples containing high concentrations of water-soluble materials, suspended solids, high boiling compounds or organohalides, it may be necessary to wash the syringe or purging device with a detergent solution, rinse with distilled water, and then dry in an 105°C oven between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bake-out and purging of the entire system may be required. A screening step is recommended to protect analytical instrumentation.

5. Safety Issues

5.1 The toxicity or carcinogenity of each reagent used in this method has not been precisely defined; each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for the information of the analyst.

6. Apparatus and Materials

6.1 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for purge-and-trap sample introduction and all required accessories, including detectors, columns, supplies, recorder, gases and syringes. A data system capable of determining peak areas is required.

6.1.2 Columns

6.1.2.1 Column 1: 105 m x 0.53 mm I.D. Restek RTX 502.2 0.3 micron film thickness, or equivalent.

6.1.2.2 Other columns such as 30 m x 0.53 mm DB-5 may be used - capillary columns are recommended to achieve necessary resolution. At a minimum, the column should resolve 2-methylpentane from the methanol solvent front in a 25 mg/kg LCS standard and should resolve ethylbenzene from m/p-xylenes. Some columns may require subambient cooling to achieve these guidelines.

6.1.3 Detector: Flame ionization detector (FID), or FID in series with a photoionization detector (PID).

6.2 Syringes: 5 mL Luerlock glass hypodermic and a 5 mL gas-tight syringe with shutoff valve.

6.2.1 For purging large sample volumes for low detection limit analysis of aqueous sample for petroleum products, 25 or 50 mL syringes may be used. Subsequently, substitute the appropriate volume in the method wherever 5 mL is stated.

6.3 Volumetric flask: 10 mL, 50 mL, 100 mL, 500 mL and 1000 mL with a ground-glass stopper.

6.4 Microsyringes: 1 uL, 5 uL, 10 uL, 25 uL, 100 uL, 250 uL, 500 uL and 1000 uL.

6.5 Syringe valve: Two-way, with luer ends (three each), if applicable to the purging device.

6.6 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g, and a top-loading balance capable of weighing to the nearest 0.1 g.

6.7 Glass scintillation vials: 20 mL, with screw-caps/crimp caps and Teflon liners or glass culture tubes with a screw-cap and Teflon liner, or equivalent.

6.8 Spatula: Stainless steel.

6.9 Disposable pipets: Pasteur.

6.10 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap and the desorber. Several complete devices are commercially available.

6.10.1 The recommended purging chamber is designed to accept 6 mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1 meets these design criteria. Alternate sample purge devices may be used, provided equivalent performance is demonstrated.

6.10.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105". Starting from the inlet, the trap must be packed with the following adsorbents: 1/2 of 2,6-diphenylene oxide polymer, 1/3 of silica gel and 1/2 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap (see Figures 2 and 3). Since only compounds boiling above 35°C are to be analyzed by this method, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Prior to initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow

of at least 20 mL/min. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min. at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

6.10.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake-out mode. The desorber design illustrated in Figures 2 and 3 meet these criteria.

6.10.4 Another alternate trap uses 7.6 cm Carbopack B and 1.3 cm Carbosieve S-III (Supelco Cat# 2-0321R). This trap should be desorbed at 240°C and baked to 300°C.

6.10.5 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 4 and 5.

6.10.6 Trap Packing Materials

6.10.6.1 2,6-Diphenylene oxide polymer: 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

6.10.6.2 Methyl silicone packing: OV-1 (3%) on Chromosorb-W, 60.80 mesh or equivalent.

6.10.6.3 Silica gel: 35/60 mesh, Davison, grade 15 or equivalent.

6.10.6.4 Coconut charcoal: Prepare from Barnebey Cheney, CA-580-26 lot #m-2649, by crushing through 26 mesh screen.

7. Reagents

7.1 Reagent Water: Carbon-filtered water purged with helium prior to use.

7.2 Gasoline Control Standards: One reference standard is API PS-6 gasoline, a characterized gasoline used in petroleum research. (Major components in Table 2). Other gasolines of similar composition can be used if they are thoroughly evaluated by the laboratory.

7.3 Gasoline Component Standard: The 10 component quantification standard which also serves as the quantification range (retention time window defining mix) standard. The components and concentration of the 10000 ug/mL stock solution are in Table 3. The standard is prepared by the procedures in 7.4 an 7.5.

7.4 Stock Standards: Prepare a stock standard for the individual gasoline component standards in methanol at approximately 20 mg/mL. The gasoline component standard should be prepared at the concentrations shown in Table 3. Also, a stock gasoline control standard should be prepared.

7.4.1 Place about 8 mL of methanol in a 10 mL tared ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min. or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.4.2 Using a 25 uL syringe, immediately add appropriate amounts of each gasoline component to the flask. The liquid must fall directly into the alcohol without contacting the neck of

the flask. For the gasoline control standard (using a separate flask), immediately add approximately 125 ul of gasoline to the flask; then reweigh.

7.4.3 Dilute to volume, stopper, and then mix by inverting the flask three times. Calculate the concentration in micrograms per liter (ug/L) for either standard. When compound purity is assayed to be 96% or greater, the volume may be used without correction to calculate he concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.4.4 Transfer the stock standard solution into a Teflon-sealed screw-cap/crimp cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

7.4.5 Standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

7.5 Calibration Standards: Calibration standards at a minimum of five concentration levels are prepared in reagent water from the stock standards. One of the concentration levels should be at a concentration near the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. See 9.3.2.

7.6 Internal Standard: Due to potential interferences, the internal standard is not recommended for FID quantification.

7.7 Surrogate Control Standard (SCS): The analyst should monitor both the performance of the analytical system and the effectiveness of the method of dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two surrogate compounds, bromofluorobenzene or trifluorotoluene. Prepare a surrogate spiking solution at 250 ug/mL of the surrogate in methanol. Add 1.0 uL of this surrogate spiking solution directly into the 5 mL syringe with every water sample, low level soil and reference standard analyzed. Surrogate spike solution is added to high level soil samples during the extraction step (see 9.5.1). Other appropriate surrogates may be used (i.e. Isopropyl Toluene).

7.8 Laboratory Control Sample (LCS) Standard: From the stock PS-6 gasoline standard or other appropriate gasoline control standards (Section 7.4), addition of the following amounts yields the indicated concentrations:

10 uL added to 100 uL water: 1 mg/L
0.5 uL added to 5 g soil: 1 mg/kg

8. Sample Collection, Preservation and Handling

8.1 Aqueous samples should be collected in triplicate without agitation and without headspace in contaminant-free glass 40 mL vials with Teflon-lined septa in the caps. The Teflon layer must contact the sample. Sample vials should contain 200 uL of 50% HCl as a preservative for aromatic analytes. Refrigerate samples at 4°C after collection.

8.2 Soil should be collected in a 4 oz. wide mouth glass jar with a Teflon-lined septa cap. The soil should be disturbed as little as possible and the containers filled as full as possible. Refrigerate all samples at 4°C after collection. Soils for GRO must be analyzed within 14 days of the date collected.

9. Procedure

9.1 Volatile compounds are introduced into the gas chromatograph by purge-and-trap. Purge-and-trap may be used directly on ground water samples. Soils and solids can be analyzed directly or by the methanol extraction procedure, depending upon level of contamination. It is highly recommended that all samples be screened prior to analysis. This screening step may be analysis of a solid sample's methanol extract (diluted), the headspace method (SW-846 Method 3810), or the hexadecane extraction and screening method (SW-846 Method 3820).

9.2 Gas Chromatography conditions (recommended)

9.2.1 Column 1: Set helium column flow to 10 mL/min. Set column temperature to 35°C for 10 min, then 4°C/min to 180°C, then 40°C/min to 220°C and hold for 12.75 min. Conditions may be altered to improve resolution of gasoline range organics.

9.2.2 Other columns-set GC conditions to meet the criteria in 6.1.2.2.

9.3 Calibration

9.3.1 Prepare final solutions containing required concentrations of calibration standards, including surrogate standards, directly in the 5 mL glass syringe. Add the aliquot of calibration solution directly to the reagent water in the glass syringe by inserting the needle through the syringe end. When discharging the contents of the microsyringe, be sure that the end of the syringe needle is well beneath the surface of the reagent water. Attach the 2-way syringe valve to the syringe and then inject the standard into the purge vessel through the two way valve. Proceed with purge-and-trap analysis procedure.

9.3.2 Run the gasoline component standard at a minimum of five concentration levels above the detection limits and covering the expected range of samples or the linear range of the instrument. For the FID quantification of a multicomponent product such as gasoline, the linear range is related to the areas of individual components.

9.3.3 Inject each calibration standard utilizing the purge-and-trap. Tabulate area response for the ten components against mass injected. The results can be used to prepare a calibration curve for the detector. Alternately, the ratio of the amount injected to the response, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the per cent relative standard deviation (%RSD) of the calibration factor is less than 25% over the working range, linearity through the origin can be assumed, and the calibration factor from the midpoint continuing calibration standard can be used in place of a calibration curve.

$$\text{Calibration Factor} = \frac{\text{Standard Amount (ng) Purged}}{\text{Total Area}}$$

9.3.4 The working calibration curve or calibration factor must be verified on each working day by the injection of a midpoint continuing calibration standard. If the response for the method standard varies from the predicted response by more than 25% a new calibration curve must be prepared.

$$\text{Percent Difference} = \frac{CF1 - CF2}{CF\ avg.} \times 100$$

where:

CF1 = Average calibration from the calibration curve.

CF2 = Calibration factor from the midpoint continuing calibration

CFavg. = (CF1 + CF2)/2

9.4 Retention Time Window and Pattern Recognition

9.4.1 Before establishing windows, be certain that the GC system is within optimum operating conditions. Make three injections of the gasoline component standard throughout the course of a 72 hour period. Serial injections over less than a 72 hour period result in retention time windows that are too tight.

9.4.2 Calculate the standard deviation of the three absolute retention times for each method standard component.

9.4.2.1 The retention time window for individual peaks is defined as plus or minus three times the standard deviation of the absolute retention time for each component. For multiresponse petroleum products, the analyst may use the retention time window but should primarily rely on pattern recognition.

9.4.2.2 In those cases where the standard deviation for a particular analyte is zero, the laboratory should use +/-0.05 min as a retention time window.

9.4.3 The Laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

9.4.4 Other organic compounds, including chlorinated solvents, ketones and ethers are measurable by this method and will be reported as gasoline range organics.

9.4.5 *Note: Although the retention time window definition (2-methylpentane to* 1,2,4-trimethylbenzene) introduces a bias, it improves precision and reduces interferences from petroleum products other than gasoline.

9.5 Gas Chromatograph Analysis

9.5.1 Water Samples: Introduce volatile compounds into the gas chromatograph using the purge-and-trap method. Add 1.OuL of surrogate standard to the sample prior to purging.

9.5.1.2 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed t come to ambient temperature, and carefully pour the sample into the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one 40 mL vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has bee analyzed properly. Filling one 5 mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

9.5.1.3 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

9.5.1.4 Dilutions may be made in volumetric flasks (10 mL to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for highly concentrated samples.

9.5.1.5 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this volume of reagent water to the flask.

9.5.1.6 Inject the proper aliquot of samples from the syringe prepared in Paragraph 9.5.1.2 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask, invert and shake three times. Repeat the above procedure for additional dilutions. Alternately the dilutions can be made directly in the glass syringe to avoid further loss of volatiles.

9.5.1.7 Fill a 5 mL syringe with diluted sample as in Paragraph 9.5.1.2.

9.5.1.8 Add 1.0 uL of surrogate spiking solution through the valve bore of the syringe; then close the valve.

9.5.1.9 Attach the syringe-syringe valve assembly to syringe valve on the purging device. Open the syringe valves and inject sample into the purging chamber.

9.5.1.10 Close both valves and purge the sample for 12 min.

9.5.1.11 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C and backflushing the trap with inert gas between 20 and 60 mL/min for 4 minutes.

9.5.1.12 While the trap is desorbing into the gas chromatograph, empty the purging chamber. Wash the chamber with minimum of two 5 mL flushes of reagent water (or methanol followed by reagent water) to avoid carryover f pollutant compounds into subsequent analyses.

9.5.1.13 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 sec; then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C. Trap temperatures up to 220°C may be employed; however, the higher temperature will shorten the useful life of the trap. After approximately 7-35 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

9.5.1.14 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has a saturated response from a compound, this analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

9.5.1.15 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

9.5.2 Sediment/soil samples: It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC analysis. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and

instrument downtime. See 9.1 for recommended screening techniques. Use the screening data to determine whether to use to the low-level method or the methanol extraction technique.

9.5.2.1 Low-level method: This is designed for samples containing low level petroleum products. It is limited to sediment/soil samples and waste that is of a similar consistency. The low-level method is based on purging a soil sample mixed with reagent water containing the surrogate and, if applicable, internal, surrogate and matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples.

9.5.2.1.1 Weigh out a 5-g sample into a purge device. Add reagent water to the purge device, cap and agigate. Add 0.5 uL of the surrogate solution to the purge device containing the sample and connect the device to the purge-and-trap system. These steps must be performed in rapid succession to avoid loss of volatiles.

9.5.2.1.2 Purge the sample 12 min. and then proceed as in 9.5.1.11 through 9.5.1.15.

9.5.3 Methanol Extraction for High Level Soil/Sediment: Weigh 10 g (wet weight) of sample into a tared 20 mL vial, using a top-loading balance. Note and record the actual weight to 0.1 gram. Quickly add 10 mL of methanol to the vial. Cap and shake for 2 min. These procedures must be performed rapidly and without interruption to avoid loss of volatile organics.

9.5.3.1 Allow sediment to settle, centrifuge if necessary. Pipet approximately 1 mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed. If not analyzed immediately, these extracts must be stored at $4^{o}C$ in the dark.

9.5.3.2 The GC system should be set up as in Section 9.0. This should be performed prior to the addition of the methanol extract to reagent water.

9.5.3.3 If a screening procedure was followed, use the estimated concentration to determine the appropriate volume of methanol extract. The maximum volume of methanol is 100 uL per 100 mL of reagent water. This is due to the need to separate cleanly the methanol front from the defined retention time window of the gasoline range organics.

9.5.3.4 Calculate the approximate volume of reagent water to be added to the 100 mL volumetric flask and add slightly less than this volume of reagent water to the flask.

9.5.3.5 Inject the proper amount of extract prepared in 9.5.3 into the flask. Dilute the sample to the mark with reagent water. Cap the flask, invert and shake three times.

9.5.3.6 Follow the procedures outlined for a dilution of a water sample as in 9.5.1.7 through 9.5.1.15. Analyze all reagent blanks on the same instrument as that used for the samples. The reagent blank should contain an aliquot of the methanol used to extract the sample.

9.5.4 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with continuing calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

9.5.5 If the responses exceed the linear range of the systems, use a smaller amount of sample.

9.5.6 The calibration factor for the gasoline range organics must not exceed +/-25% when compared to the initial standard of the analysis sequence. When this criteria is exceeded,

inspect the GC necessary prior to recalibration and proceeding with sample exceeding QC criteria must be reanalyzed.

9.6 Calculations

9.6.1 The concentration of Gasoline Range Organics in the sample is determined by calculating the absolute weight of analyte purged, from a summation of peak response for all chromatographic peaks eluting between 2-methylpentane and 1,2,4-trimethylbenzene, using the calibration curve or calibration factor determined in 9.3.3. Refer to 9.4 (Retention Time Windows and Pattern Matching). The concentration of Gasoline Range Organics is calculated as follows:

Aqueous or soil samples:

$$Cs\ (ng/mL \text{ or } ng/g) = \frac{AX}{Vs \text{ or } Ms} \times CF \times D$$

Where:

Cs = Concentration of Gasoline Range Organics.

Ax = Response for the Gasoline Range Organics in the sample, units in area.

CF = Calibration Factor from continuing calibration, units = ng/area.

D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D=1, dimensionless.

Vs = Volume of sample purged, mL.

Ms = Mass of sample purged, g.

10. Quality Control

10.1 The laboratory must, on an ongoing basis, demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control. This should include the analysis of QC check samples plus the calculation of average recovery and the standard deviation of the recovery as outlined in Method 8000, Section 8.0.

10.2 After successful calibration (Section 9.3), analyze a Surrogate Control Sample. This standard is also the reagent blank sample and is analyzed with every analytical batch or sequence. The surrogate recovery should be within established limits (Table 4) and the sample should not have Gasoline Range Organics above the practical qualification limit.

10.3 Every batch or 20 samples, duplicate Laboratory Control Samples must be analyzed. The accuracy and precision of the Duplicate standards must be within established limits. (Table 4).

10.4 If any of the criteria is 10.2 and 10.3 are not met, the problem must be corrected before samples are analyzed.

10.5 Calculate sure surrogate standard recovery in each sample. If recoveries are outside established limits, verify calculations, dilutions, and standard solutions. Verify instrument performance.

10.5.1 High recoveries may be due to a coeluting matrix interference-examine the the sample chromatography.

10.5.2 Low recoveries may be due to the sample matrix.

10.5.3. Low recoveries may be due to a poor purge (clogged purge tube). If this is suspected, reanalyze the sample while observing the purge tube.

10.6 Field blanks, duplicates and matrix spikes are recommended for specific sampling programs.

11. Method Performance

11.1 The average recovery of gasoline from water samples spiked with 1000ppb was 68% with a Relative Standard Deviation (RSD) of 20 (n=31). The average recovery of gasoline from sediments samples spiked with 1000ppb was 75% with a Relative Standard Deviation (RSD) of 24 (n=24).

12. References

1. USEPA "SW-846 Test Methods for Evaluating Solid Waste", 3rd Edition; Methods 5030, 8000, 8015, and 8030.

2. American Petroleum Institute "Sampling and Analysis of Gasoline Range Organics in Soils", in preparation.

3. "Evaluation of Proposed Analytical Methods to Determine Total Petroleum Hydrocarbons in Soil and Groundwater" prepared by Midwest Research Institute for USEPA Office of Underground Storage Tanks, August 14, 1990.

4. ASTM "Standard Practical For Sampling Waste and Soils For Volatile Organics" Draft #1, 2/16/87.

5. Parr, J.L., G. Walters, and M. Hoffman, "Sampling and Analysis of Soils for Gasoline Range Organics" presented at First Annual West Coast Conference Hydrocarbon Contaminated Soils and Groundwater, 2/21/90.

6. American Petroleum Institute "Laboratory Study on Solubilities of Petroleum Hydrocarbons in Groundwater", August, 1085, API Publ. 4395.

7. "Leaking Underground Fuel Tank (LUFT) Field Manual," State Water Resources Control Board, State of California, Sacramento, California, May, 1988.

8. Fitzgerald, John "Onsite Analytical Screening of Gasoline Contaminated Media Using a Jar Headspace Procedure" in Petroleum Contaminated Soils, Vol. 2, 1989.

9. Senn, R.B., and M.S. Johnson, "Interpretation of Gas Chromatographic Data in Subsurface Hydrocarbon Investigations," Ground Water Monitoring Review, 1987.

10. Hughes, B.M., D.E. McKenzie, C.K. Trang, L.S.R. Minor, "Examples of the Use of an Advanced Mass Spectrometric Data Processing Environment for the Determination of Sources of Wastes" in Fifth Annual Waste Testing and Quality Assurance Symposium; USEPA, July 24-28, 1989.

11. Urban, M.J., J.S. Smith, E.K. Schultz, R.K. Dickson, "Volatile Organic Analysis for a Soil, Sediment or Waste Sample" in Fifth Annual Waste Testing and Quality Assurance Symposium; USEPA, July 24-28, 1989.

12. Siegrist, R.L., and P.D. Jenssen, "Evaluation of Sampling Method Effects on Volatile Organic Compound Measurements in Contaminated Soils", Environmental Science and Technology, Vol. 24, November 9, 1990.

TABLE 1
PURGE AND TRAP OPERATING PARAMETERS

	ANALYSIS METHOD 8020
Purge gas	Nitrogen or Helium
Purge gas flow rate (mL/min)	20-40
Purge time (min)	12.0 +/-0.1
Purge temperature	Ambient
Desorb temperature (^{o}C)	180
Backflush inert gas flow mL/min)	20-60
Desorb time	4

TABLE 2
MAJOR COMPONENTS OF API PS-6 GASOLINE

Compound	Percent Weight		
2-Methylbutane		8.72	
m-Xylene			5.66
2,2,4-Trimethylpentane		5.22	
Toluene			4.73
2-Methylbutane		3.93	
n-Butane			3.83
1,2,4-Trimethylbenzene		3.26	
n-Pentane			3.11
2,3,4-Trimethylpentane		2.99	
2,3,4-Trimethylpentane		2.85	
3-methylpentane		2.36	
o-Xylene			2.27
Ethylbenzene		2.00	
Benzene			1.94
p-Xylene			1.72
2,3-Dimethylbutane	1.66		
n-Hexane		1.58	
1-Methyl, 3-ethylbenzene		1.54	
1-Methyl, 4-ethylbenzene		1.54	
3-Methylhexane			1.30

Reference (6)

TABLE 3
GASOLINE COMPONENT STANDARD AND CONCENTRATIONS

Component	Concentration, (ug/mL)
2-Methylpentane	1500
2,2,4-Trimethylpentane	1500
Heptane	500
Benzene	500
Toluene	1500
Ethylbenzene	500
m-Xylene	1000
p-Xylene	1000
o-Xylene	1000
1,2,4-Trimethylbenzene	1000
	10000 ug/mL Total

TABLE 4
ACCEPTANCE CRITERIA FOR LABORATORY QUALITY CONTROL CHECKS

Analyte	Spike Concentration		Control Limits Relative
Laboratory Control Sample	Water mg/L	%Rec	%Difference
Gasoline Range Organics	1.0	50-100	20
Surrogate Control Sample			
Isopropyltoluene	0.05	50-150	

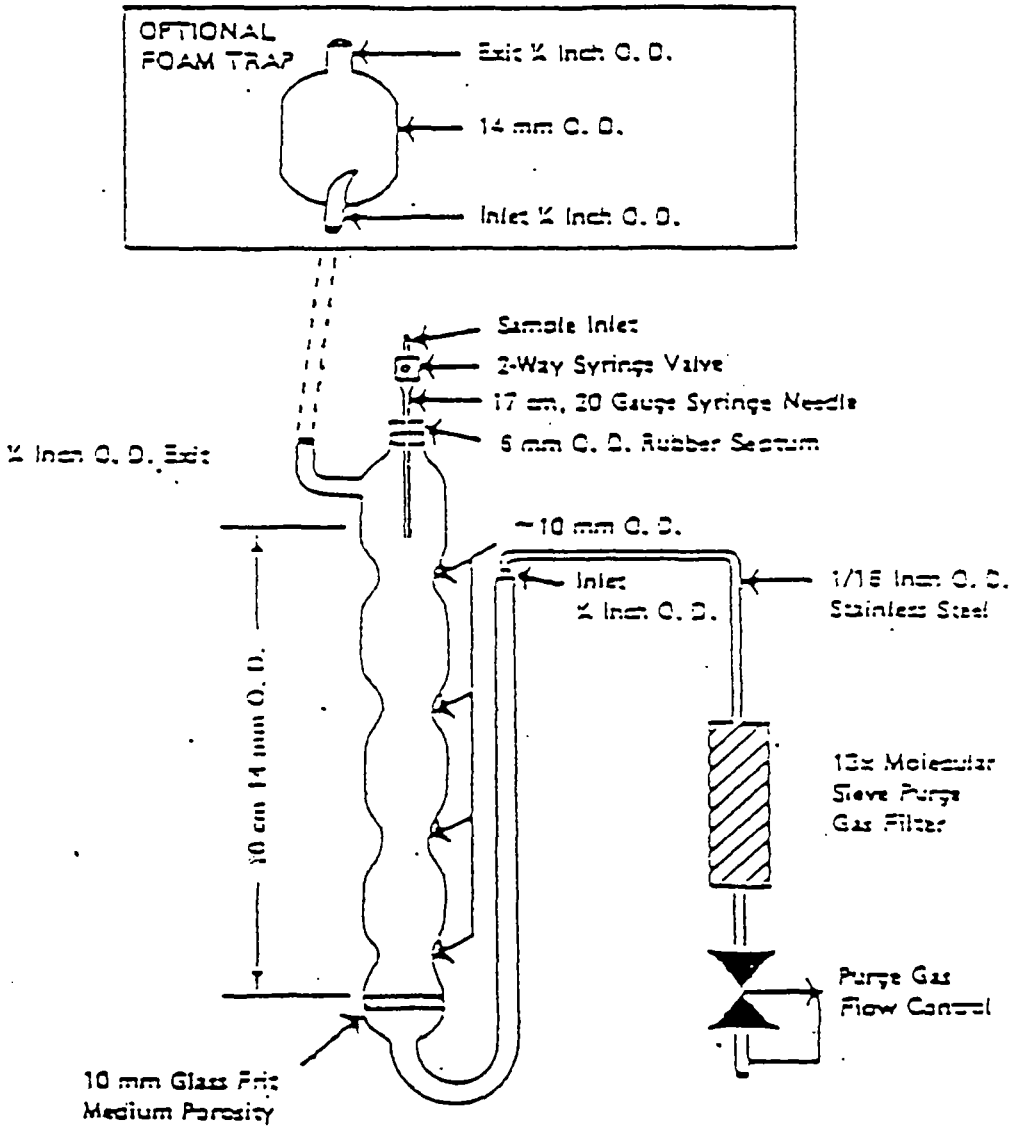


Figure 1. Purging chamber.

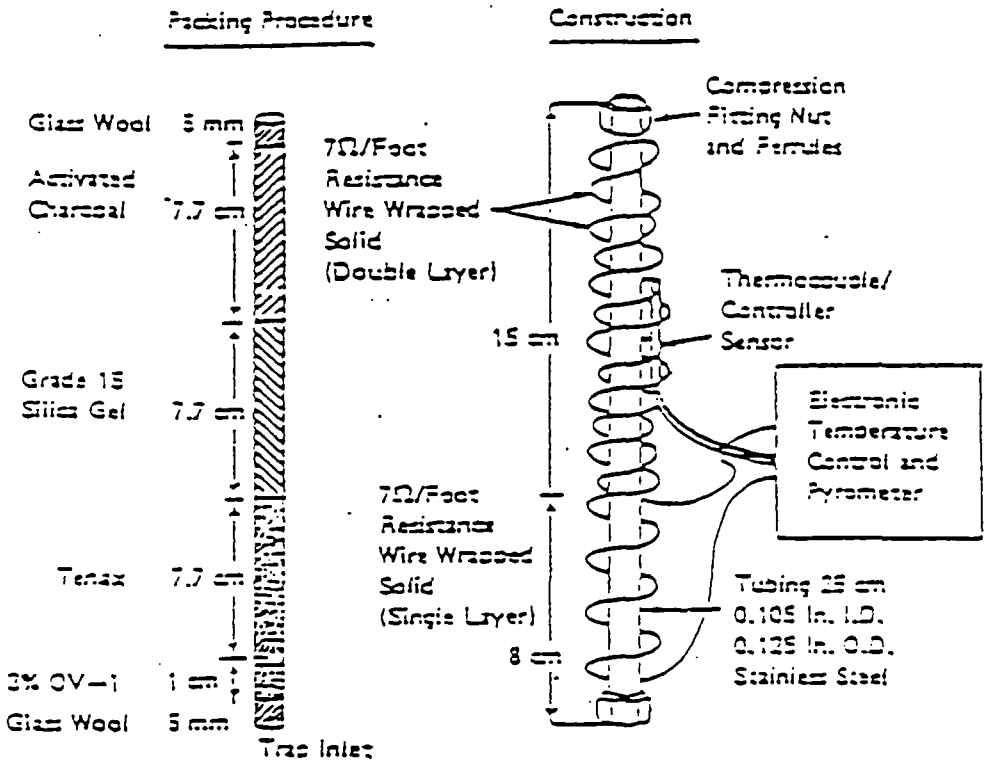


Figure 2. Trap packings and construction

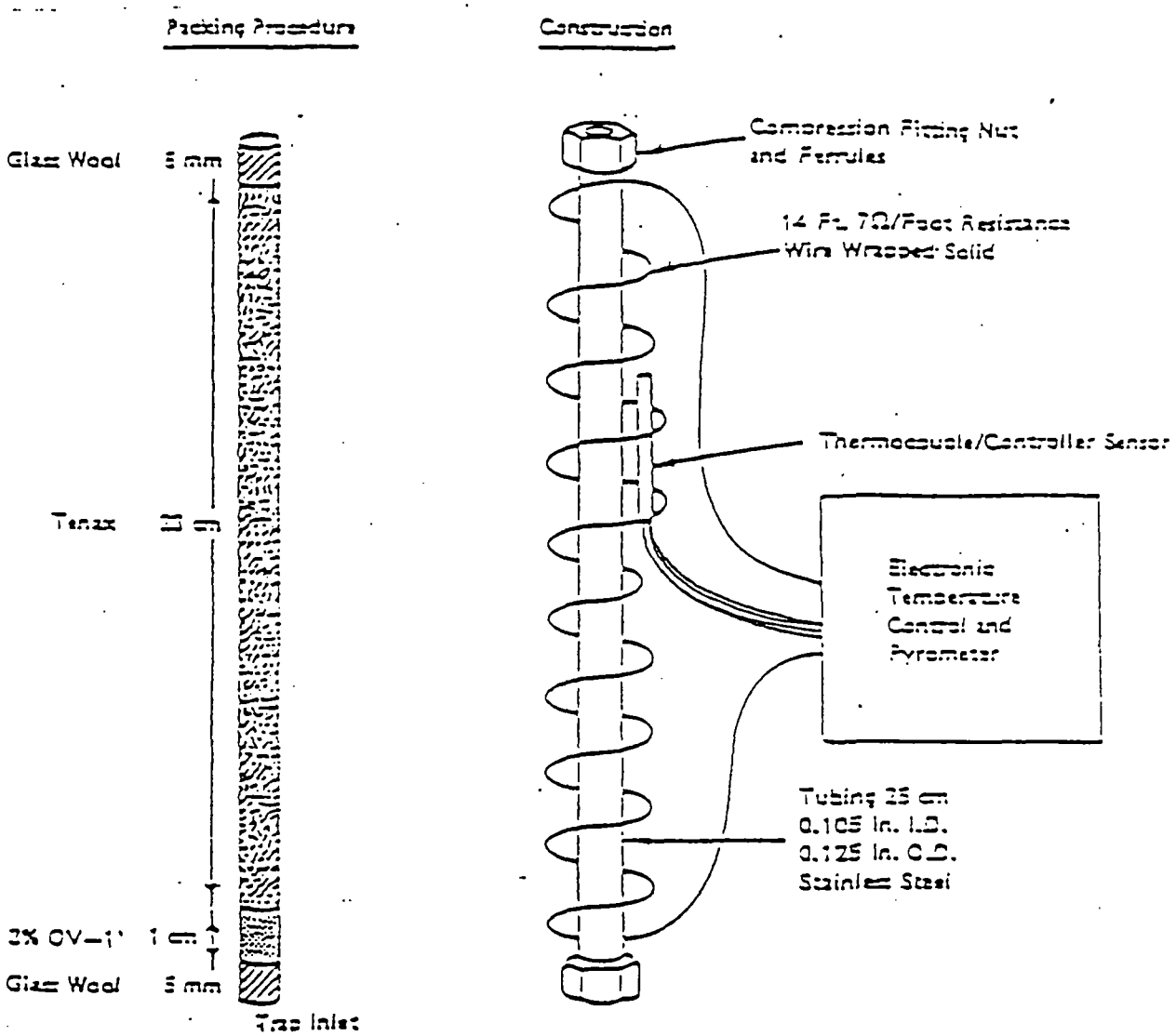


Figure 3. Trap packing and construction

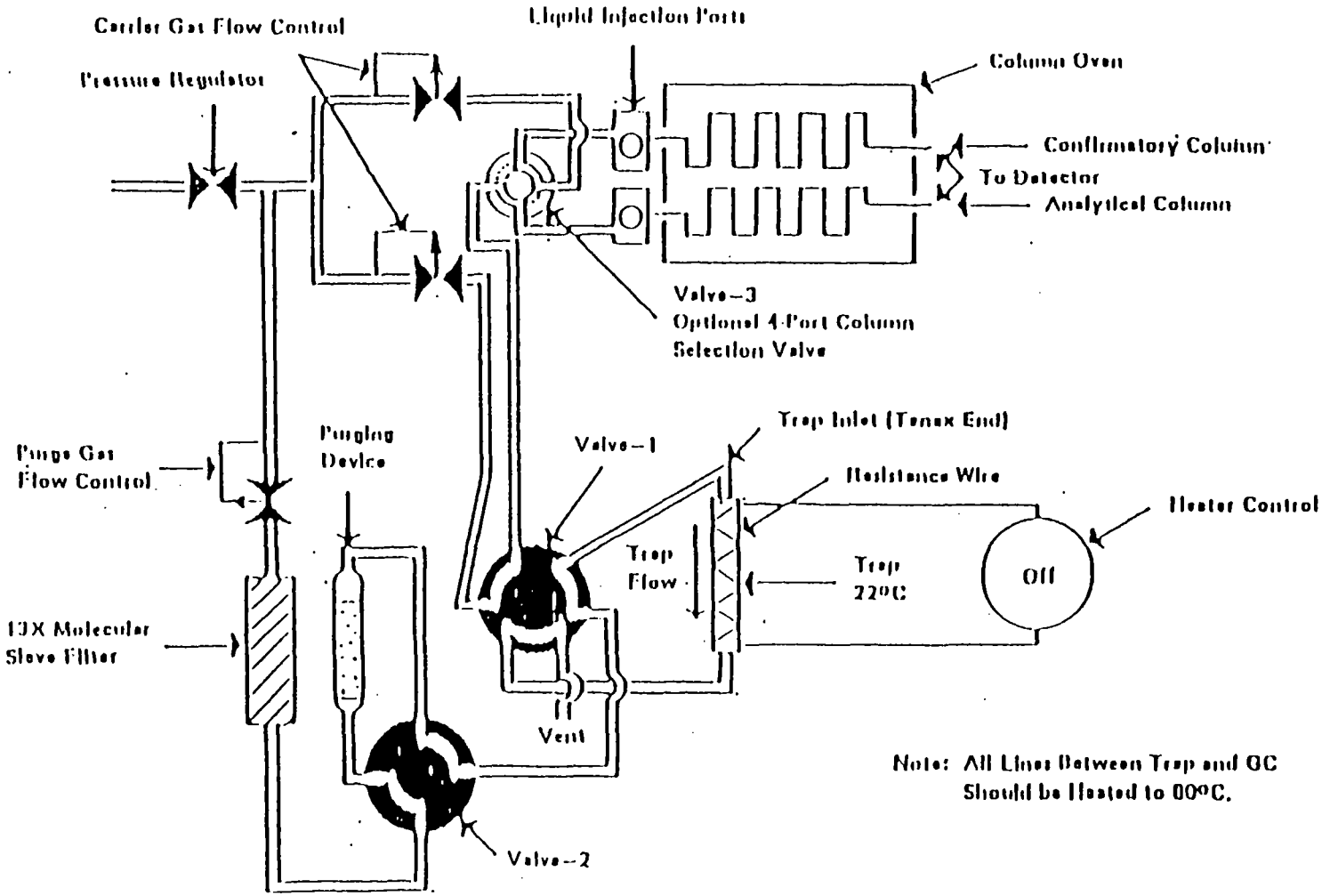


Figure 4. Purge-and-trap system, purge-sorb mode

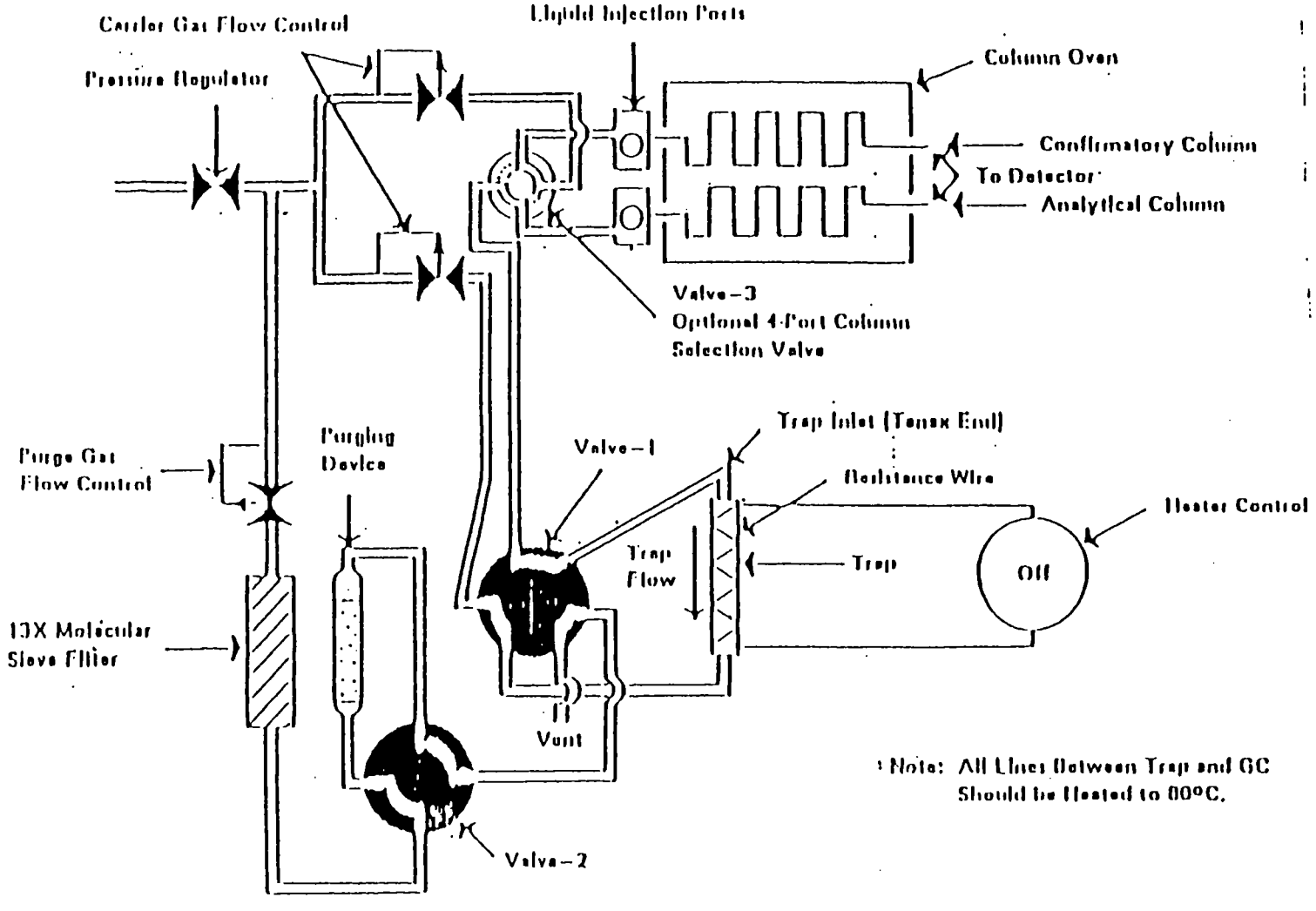


Figure 5. Purge-and-trap system, desorb mode.

STANDARD OPERATING PROCEDURE

Diesel Range Organics

SOP NUMBER: HO-0-029

AUTHOR: Matt Hearne

EFFECTIVE DATE: January 23, 1997

APPROVAL

Laboratory Operations Manager _____ Date _____

Quality Assurance Officer _____ Date 1/23/97

SOP for the Analysis of Diesel Range Organics

Purpose/Applicability

The purpose of this SOP is to describe the procedures used to determine the concentration of diesel range organics in sample extracts. Diesel range organics are defined as any chromatographic peak that elutes during the retention time window as determined by the standard. The standard is a ten-component paraffins mixture ranging from decane to octacosane prepared in methylene chloride. This SOP references SW-846 method 8015, and has been modified to be applicable to the compounds of interest.

Method Summary

The procedure involves calibrating the GC with a ten-component paraffins mixture at a minimum of five levels and using the average response factor generated by the curve to determine the concentration of the diesel range organics in sample extracts. The sample extracts will be prepared using method 3510 for aqueous samples and 3550 for soils. The analysis of the extracts will be done by direct injection GC/FID. The working range of the instrument is from 50 ng/ul to 2000 ng/ul.

This procedure can be applied to a number of different matrices including water, waste water, soil and sludges.

Safety

Safety concerns fall into three categories: exposure to toxic organic chemicals; burns from hot instruments; and injuries from sharp syringes or broken glassware.

Chemical Exposure

The working solvent used in this procedure is methylene chloride. Care should be exercised when using it, and all work in preparing the samples should be done under a fume hood. Also, the fact that this analysis involves the determination of hydrocarbons in a concentrated extract, extreme care should be used in the handling of all sample extracts.

Burns

There are several sources for thermal burns when following this procedure, and the analyst needs to exercise due caution. The GC oven reaches operating temperatures approaching 300 degrees C. The injector temperature is held at 260 degrees, and the detector at 310 deg C.

Injuries

Broken glass always presents a safety concern in the lab. In addition, the frequent use of syringes in this procedure carries with it the risk of puncture wounds and even inadvertent injection. The analyst must be careful.

Sample storage and handling

All sample extracts will be stored at 4 degrees or less until analysis. Before analysis or preparation of sample extracts, allow the extracts to equilibrate to room temperature.

Equipment

The following equipment will be used during the analysis, or their equivalents:

1. HP 5890 GC with FID
2. HP 7673A autosampler
3. RTX-5 30m x 0.32mm column
4. 2ml autosampler vials with crimp tops or screw caps
5. Pasteur pipettes
6. Assorted syringes from 25 ul to 1000 ul

Reagents

All standards and sample dilutions will be prepared in HPLC grade methylene chloride. The calibration standard used is a 10 component paraffin mixture ranging from decane (C10) to octacosane (C28). The Protocol catalog description is NUS-DIEL at an initial concentration of 10,000 ug/ml. The surrogate used is n-pentacosane supplied by Chem-Service, and the spiking mixture is diesel fuel #2 supplied by Restek. These standards may be purchased from the suppliers above or an equivalent source.

Procedure

Calibration

Initial calibration will consist of five concentrations of the NUS-DIEL standard encompassing the working range of the instrument, nominally from 50 ng/ul to 2000 ng/ul. The analytical method to be used is called FORCE. After each standard has been analyzed the area of each paraffin will be integrated and summed together. An average calibration factor is calculated for each concentration and a calibration curve generated. The calibration curve will be considered passing if the percent relative standard deviation (RSD) of the calibration factors is less than 20%, or if the correlation coefficient is at least 0.995.

The method used for continuing calibrations on instrument 0030GC is called FORCE. This method uses an integration event that forces the output to include a sum of the total area for all ten compounds. This area is multiplied by the average calibration factor generated in the initial calibration to give the final result. The percent difference from the final result and the expected value must be less than 15%.

Analysis

All samples, blanks, laboratory control samples, matrix spikes and matrix spike duplicates will be analyzed on 0030GC using the method called TPHDRO. This method uses

all of the same parameters used for the calibration, but sums the total area of all hydrocarbons that elute during the chromatographic time frame determined by the first and last paraffin in the standard. The total area of the analysis is multiplied by the calibration factor determined in the initial calibration. The result will be calculated as ug/ml. Any dilution must be taken into account and all results will be reported in mg/L or mg/kg.

Quality Control

The quality control will consist of method blanks, laboratory control samples, matrix spike and matrix spike duplicates. There is only one surrogate compound used in this procedure, n-pentacosane, and is spiked into all samples, blanks and quality control standards.

The method blanks must have a total amount of diesel range organics less than the lowest standard used in the initial calibration which is used in determining reporting limits.

The laboratory control samples will be spiked with diesel fuel #2 at an extract concentration of 500 ug/ml. The acceptance criteria for it is determined from control charts of twenty or more recoveries of diesel in laboratory control samples. A copy of these limits is include at the back of this procedure. A method blank and LCS will be extracted with each batch of samples up to twenty.

The matrix spike and duplicate samples will be spiked with diesel fuel #2 at an extract concentration of 500 ug/ml. The results from each set of matrix spike and duplicate should be recorded in a control chart. There will be one set of MS/MSD for each batch of twenty samples.

All sample extracts will be spiked with n-pentacosane as the surrogate. The method used in the calculation of the surrogate recovery for instrument 0030GC is TPHSURR. The criteria for surrogate recoveries are derived from control charts. A copy of these limits is included at the end of this procedure.

Calculations

The reported results will be calculated as follows:

Water samples:

$$\frac{R_i\ (ug/ml) \times V_f\ (ml)}{V_i\ (ml)}$$

where R_i is the observed instrument result
V_f is the final volume of the extract
V_i is the initial volume of the sample

Final results will be reported as mg/L

Soil samples:

$$\frac{R_i\ (ug/ml) \times V_f\ (ml)}{V_i\ (g)}$$

where R_i is the observed instrument result
V_f is the final volume of the extract
V_i is the initial volume of the sample

Final results will be reported as mg/kg

References

SW-846 method 8015

PACE ANALYTICAL SERVICES, INCORPORATED
HOUSTON LABORATORY

STANDARD OPERATING PROCEDURE

Analysis of Sample Extracts for Semivolatile Compounds

SOP NUMBER	HO-O-026
AUTHOR	Matt Hearne
Effective Date	January 23, 1997
Supersedes	First Issue

APPROVAL

Department Supervisor — Date: 1/23/97

Quality Assurance Officer — Date: 1/23/97

TABLE OF CONTENTS

Analysis of Sample Extracts for Semivolatile Compounds

I. Purpose and Applicability

This method is used to determine the concentration of various organic semivolatile compounds using SW-846 Method 8000 as a guideline. Table 1 indicates compounds that may be determined by this method.

II. Summary of Method

This method provides gas chromatographic conditions for detection of ppm levels of certain organic semivolatile compounds. Both neat and diluted organic liquids may be analyzed by direct injection. A 0.5 to 2.0ul sample is injected into the gas chromatograph, and compounds in the GC effluent are detected by an ion trap mass spectrometer.

The sensitivity of this Method usually depends on the level of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, this method may also be performed on samples that have undergone cleanup.

III. Interferences

Interferences may be caused by the presence of high levels of non-target compounds which are extracted along with the target analytes. The effects of these interferences are normally reduced through dilution of the sample extracts or reducing the amount of sample extracted. Some types of interferences may be reduced using GPC cleanup.

IV. Safety

This procedure requires the use of materials, which when handled improperly, pose potential health risk to everyone in the laboratory. It is important that all necessary safety precautions are followed. This includes the use of properly operating fume hoods, appropriate gloves, protective eyewear, lab coats, and respiratory protection as necessary. Users of this procedure must be cognizant of inherent syringe hazards, proper disposal procedures for contaminated materials, and appropriate segregation of waste. Everyone involved in the procedure must be familiar with the MSDS for solvents and chemicals used. Any additional information can be received by consulting with your Chemical Hygiene Plan.

V. Responsibility

A. Personnel

1. All personnel involved with sample preparation and analysis are responsible for adherence to this Standard Operating Procedure (SOP).

2. Personnel are responsible for ensuring that any deviations to this SOP are reported.

3. All personnel are responsible for notifying the department manager/supervisor of any required revisions to the SOP.

B. Department manager/supervisor

1. The department manager/supervisor is responsible for ensuring adherence to this SOP.

2. The department manager/supervisor is responsible for performing an annual review of the SOP and reporting any required revisions to the Quality Assurance Office.

C. Quality assurance office (QAO)

1. The QAO is responsible for conducting periodic laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Regional Management and Corporate Quality.

2. The QAO is responsible for ensuring that all revisions to the SOP are implemented.

3. The QAO is responsible for determining distribution of and maintaining document control for this SOP.

VI. Reviews/revisions

A. This SOP will be reviewed on an annual basis at a minimum.

B. At the time of review, any required revisions will be incorporated.

C. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

VII. Distribution

This SQP will be issued to the GC lab and any other areas deemed appropriate by the QAO.

VIII. Equipment and Supplies

A. Gas Chromatographs:
Varian 3400 GC or equivalent

B. Columns:
XTI-5 0.25mm x 30M film thickness of 0.25um
or equivalent

C. Detector:
Ion Trap Detector

D. Carrier gas:
Helium. Carrier flow is approximately 5mls/min.

E. Solvents:
Methylene Chloride (pesticide quality or equivalent)

IX. Standards

Sources: Supelco,Restek, Protocol, Chem Service or equivalents

Stock standards are currently purchased from Supelco in two separate mixes but may be purchased from any of the othe suppliers listed above. The mixes with their list of analytes and concentration are in the table below:

EPA TCLP Base-Neutrals Mix-B:	conc. (ug/ml)
2-Nitroanaline	1000
bis(2-chloroethyl)ether	1000
Nitrobenzene	1000
Pyridine	1000

Surrogates (Restek):

B/N Surrogate Mix	
Nitrobenzene-d5	5000

X. Calibration Standards

Calibration Standards are made from dilutions of the stock standards above and combined to form one calibration mix. The dilutions made should bracket the working range of the instrument.
All standard mixes are made up in methylene chloride and stored in the refrigerator and kept only 6 months or whenever the calibration standard shows signs of degradation.

XI. Calibration

The internl standard calibration procedure is used. Each analyte of interest is run at a minimum of 5 different concentrations, a calibration curve is constructed and the %RSD for each component are calculated and must not exceed 20%. The concentration of the calibration standard should define the working range of the specific instrument. See Table 1 for an example of a typical calibration sequence including concentrations.

Continuing calibrations must be verified every 10 samples and the %RPD for each analyte of interest must not exceed 15%. A midpoint concentration of all analytes of interest must be included. If any analyte of interest fails the criteria, then all samples analyzed after the last passing calibration must be reanalyzed.

XII. Retention Time Windows

Whenever a new column is installed into the GC, retention time windows must be established. The windows are initially established by monitoring and recording the rention times of the peaks. The data are collected from three separate injections of standards over a 72 hour period of time. The retention time window is calculated as plus or minus three times the standard deviation of the retention time for each peak. For compounds that have standard deviations of retention time that

are extremely small, the retention time window from a compound that it is close to, and similar with, should be substituted.

For daily analysis, the absolute retention time from the standards run within that 12 hour period of time will be used as the midpoint of the window. Tentative identification of target compounds will be based on peaks that elute during the daily retention time window and the mass spectra produced by the detector.

XIII. Analytical Sequence

Table 2 shows a typical sequence of analysis beginning with an initial calibration, sample analyses, and continuing calibration, and closing calibration.

XIV. Quality Control

A. Surrogates Recoveries

Calculate the surrogate recoveries for all the samples, blanks, LCS's, and matrix spikes. The recoveries should fall within the acceptance limits established by historical data. The control limits are defined as the mean plus or minus three times the standard deviation of the recovery for each surrogate collected over a period of time.
If the recoveries of both surrogates fall outside the control limits, check the instrument performance and/or reanalyze the samples in question. If the surrogate recoveries are still out of control, then re-extract the samples which were out of the surrogate control limits. See Figure 4 for a listing of the surrogate control limits.

B. Method Blanks

A method blank is prepared and analyzed with every batch of up to 20 samples extracted. If any target compounds are detected in the method blank at or above the reporting limit, all samples with positive hits for those compounds must be re-extracted.

C. LCS Recoveries

A Lab Control Sample (LCS) prepared from a source separate from the calibration standards is run with every extracted batch of samples. The LCS control limits are calculated from historical data. If the LCS results are outside the control limits, corrective action must be taken. The analyst should first check the instrument performance, followed by reanalysis of the LCS and possibly re-extraction of all samples associated with it. See Figure 5 for a listing of the LCS control limits.

D. MS/MSDs

A matrix spike and matrix spike duplicate are extracted at a 5% frequency or as specified by the project. If the recovery of any compound spiked does not fall within the control limits established for the LCS, that compound must demonstrate acceptable recovery in the associated LCS, and the data flagged as indicative of possible matrix interference.

IX. Applicable Documents/References

Test Methods for Evaluating Solid Waste Physical/Chemical

Methods, US EPA SW 846, 3rd edition: Method 8081A.

TABLE I

Spike Solution Concentration Levels
(ug/mL)

Semivolatiles	Level
bis(2-chloroethyl)ether	10.0
2-Nitroaniline	10.0
N-nitrosodi-n-propylamine	10.0
Nitrobenzene	10.0

TABLE II

Calibration and Analytical Sequence

Std. (level #1)
Std. (level #2)
Std. (level #3)
Std. (level #4)
Std. (level #5)
Samples (10 total)
Std. (mid-pt calibration level)
Samples (10 total)
Std. (mid-pt calibration level)

Note: Method Blanks, LCS's, MS/MSD's are included in the total of 10 samples between calibration checks; instrument blanks are not. Calibration check standards must be analyzed at a minimum every 12 hours of sample analysis.

STANDARD OPERATING PROCEDURE

MERCURY BY COLD VAPOR AA - SW846
METHOD 7470A, 7471A

SOP NUMBER	HO-I-036-C
AUTHOR	DAVID ROSE / JAN WALRATH
EFFECTIVE DATE	JUNE 2, 1995

APPROVAL

Jan Walrath 6/2/95
Metals Supervisor Date

Russell Morgan 6-2-95
Laboratory Inorganic Manager Date

6-5-95
Quality Assurance Officer Date

6-2-95
Laboratory General Manager Date

CONTROLLED COPY
METALS LAB

I. PURPOSE / APPLICATION / SAFETY

The purpose of this procedure is to establish a method compliant with methods SW846-7470A and -7471A for the determination of mercury using cold vapor techniques. This procedure is applicable to inorganic and organic forms of mercury in waters and soils. Mercury fumes are highly toxic. Care should be taken to insure proper ventilation of analysis area. Standard laboratory safety practices must be followed (see safety manual for guidelines).

II. SUMMARY

The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental molecule and aerated from a solution in a closed system. The mercury vapor passes through a cell positioned in the light of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration determined linearly.

III. RESPONSIBILITIES

QUALITY ASSURANCE OFFICER

The Quality Assurance Officer (QAO) has overall responsibility for monitoring implementation of and adherence to the policies and procedures set forth in this document. The QAO will periodically audit the facility to monitor adherence and the results will be reported to Laboratory Management and Corporate Quality.

INORGANIC LABORATORY MANAGER / METALS SUPERVISOR

The manager/supervisor has responsibility to ensure adherence to this SOP and will ensure that this SOP is periodically reviewed notifying the QAO as required.

ANALYST

The analyst responsibility is to follow all procedures in this SOP and to report and document any deviations to the procedures set forth in this SOP.

IV. PREPARATION / DIGESTION

DISCUSSION - INTERFERENCES:
Potassium permanganate and potassium persulfate are added during digestion of samples to break down organo-mercury compounds that would otherwise not respond to the cold vapor technique. A heating step is required for methyl mercuric chloride when present in or spiked to a natural system. Possible sulfide interferences are also eliminated by the addition of potassium permanganate. Concentrations as high as 20 µg/L of sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water. Sea waters, brine and industrial effluents high in chlorides require additional permanganate (as much as 25 mL). During the oxidation step, chlorides are converted to free chlorine that will also absorb radiation of 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride reagent (25 mL). Both inorganic and organic mercury spikes have been quantitatively recovered from the sea water using this technique.

EQUIPMENT:
Wheaton 300 mL BOD bottles or equivalent
100 mL graduated cylinders
Water bath or equivalent
Volumetric class A pipettes, various sizes
Volumetric flasks, various sizes, class A
Analytical balance: Sartorius or equivalent
Eppendorf mechanical pipets, various sizes

REAGENTS:
Deionized water (DI) - Water will be monitored for impurities (ASTM Type II)
Concentrated nitric acid (HNO_3) - Reagent grade or better
Concentrated sulfuric acid (H_2SO_4) - Reagent grade or better
Potassium permanganate ($KMnO_4$): Dissolve 25g $KMnO_4$ in DI water and bring to final volume of 500 ml.
Potassium persulfate ($K_2S_2O_8$): Dissolve 40g $K_2S_2O_8$ in DI water (warm to dissolve all crystals) and bring to final volume of 500 mL.
Stannous chloride ($SnCl_2 2H_2O$): Dissolve 50g $SnCl_2 2H_2O$ in 250 mL 1.0 N H_2SO_4 and bring to a final volume of 500 mL with DI water. This solution is a suspension and should be stirred continually during use.
Sodium Chloride - Hydroxylamine Hydrochloride: Dissolve 60g NaCl and 60g Hydroxyalmine Hydrochloride in DI water and bring to a final volume of 500 ml.
Aqua Regia: Prepare immediately before use by carefully adding three volumes of conc. HCl to one volume of conc. HNO_3.

STANDARDS:
Mercury stock solution - 1000ppm NIST traceable standard
1000ppb - Mercury intermediate standard: Dilute 1.0 ml of 1000ppm stock standard to 1000 ml with DI water + 1.5ml HNO3 to preserve.
100ppb - Mercury working standard: Dilute 10.0 ml of 1000ppb working standard to 1000 ml with DI water + 1.5ml HNO3 to preserve.

Working linear curve for preparation/digestion/analysis:
The correlation coefficient of the curve should bo 0.995 or greater.

Concentration - ppb	Volume of 100ppb	-per 100ml for aqueous matix -per bottle for solid matrix
0.0	0.0 ml	
0.2 *	0.2 ml	
0.5 *	0.5 ml	
1.0	1.0 ml	
2.0 **	2.0 ml	
5.0	5.0 ml	
10.0	10.0 ml	
20.0	20.0 ml	
10.0 ***	10.0 ml ***	

* Reporting limit
** Amount added for MS/MSD and LCS-water
*** ICV/CCV made from a separate Mercury standard source

A. AQUEOUS MATRIX

Aqueous samples are preserved to a pH of <2 with HNO3 and stored at room temperature. The samples will be analyzed within 28 days of collection.

STANDARD DIGESTION:
Transfer the prepared standards into the 300 ml BOD bottles.
Add/swirl 5 mL of conc. H2SO4 and 2.5 mL of conc. HNO3 to each bottle.
Add 15 mL of KMnO4 solution to each bottle.
Let stand at least 15 minutes.
Add/swirl β mL of potassium persulfate to each bottle.
Heat for 2 hr in a water bath at 95-C then cool.
Prior to analysis, add/swirl 6 ml NaCl-hdroxylamine hydrochloride to reduce excess permanagate

SAMPLE DIGESTION:
Transfer 100 mL of sample (or an aliquot diluted to 100 mL containing >1.0g of Hg) to a 300mL BOD bottle.
Add/swirl 5 mL of conc. H2SO4 and 2.5 mL of conc. HNO3. to each bottle.
Add 15 mL of KMnO4 solution to each sample bottle. (Sewage samples may require additional permanganate. Ensure that equal amounts of KMnO4 are added to standards and blanks. Add/swirl additional portions of KMnO4 solution until the purple color persists for at least 15 min.
Add 8 mL of potassium persulfate to each bottle.
Heat for 2 hr in a water bath maintained at 95-C then cool.
Prior to analysis, add/swirl 6 ml NaCl-hydroxylamine hydrochloride to reduce excess permanganate. **Caution:** Do this addition under a hood as Cl2 could be evolved.

B. SOLID MATRIX

Solid samples are preserved/stored at 4-C (+/- 2-C). The samples will be analyzed within 28 days of collection.

STANDARD DIGESTION:
Transfer aliquots of the mercury working standard (as per table)to 300mL BOD bottles.
Add DI water to each bottle to make a total volume of 10 mL.
Add/swirl 5 mL of aqua regia.
Heat 2 minutes in a water bath at 95-C.
Cool and add 50 ml of DI water.
Add/swirl 15 mL of KMnO4 solution to each bottle.
Return bottles to the water bath for an additional 30 minutes then cool.
Prior to analysis, add/swirl 6 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce the excess permanganate.
Add 50 mL of ASTM Type II water.

SAMPLE DIGESTION:
Weigh triplicate 0.2 g portions of untreated sample and place in the bottom of a 300ml BOD bottle.
Add 5 mL of DI water.
Add/swirl 5 mL of aqua regia.
Heat 2 min in a water bath at 95-C.
Cool and add 50 mL DI water.
Add/swirl 15 mL KMnO4 solution to each sample bottle.
Return bottles to the water bath for an additional 30 min then cool.
Prior to analysis, add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. **CAUTION**: Do this addition under a hood, as Cl2 could be evolved.
Add 50 mL of ASTM Type II water.

Note: An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of conc. H2SO4 and 2 mL of conc. HNO3 are added to the triplicate 0.2 g portions of sample. Add 5 mL of saturated KMnO4 solution and cover the bottle with a piece of aluminum foil. The samples are auto-claved at 121-C and 15 lb for 15 min. Cool and dilute to a volume of 100 mL with DI water. Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate.

V. ANALYSIS: FIMS-400

DISCUSSION:
The principle of analysis using the Flow Injection Mercury System (Perkin-Elmer) is as follows. A reagent solution is introduced at a suitable point in the flow injection system. The sample undergoes a chemical reaction as it is transported through the system. The mercury must be in an ionic form in the sample solution. When the reducing agent ($SnCl_2$) mixes with the sample, the ionic mercury is converted to metallic mercury. An inert carrier gas (N_2) transports the mercury to the spectrometer. The resulting concentration is read as absorbance and is linearly derived from a calibration curve.

EQUIPMENT:
FIMS-400 with associated computer and printer

REAGENTS:
Carrier solution: 3% HCl - Dilute 30 ml of conc. HCl to 1L DI water.
Reducing agent: 1.1% $SnCl_2$ in 3% HCl - Add 22.0g $SnCl_2$-$2H_2O$ to a 2L volumetric flask. Add 60 ml conc. HCl and bring to volume.
Carrier gas: Nitrogen - zero grade (Argon may also be used).

A. INSTRUMENT PROCEDURE

COMPUTER:
Prepare the autosampler table with sample information and associated tables as per manufacturer instructions (see Appendix A for example).

Select: Method - MERCURY
Sample Information File - input run information
Name the Results Data File - usually the current date
Data Save
Print Log
Off - End Analysis

AUTOSAMPLER:
Load the standards and prepared samples according to the table.
Connect the pump windings and check that they are aligned with the correct solutions according to the manufacturer instructions.
Connect the carrier gas.
Check flow rates:

carrier gas	-	70-100 ml/min
carrier solution	-	9-11 ml/min
reductant solution	-	5-7 ml/min (half of carrier)

To start analysis, after everything has been prepared and checked, select Analyze All in the Automated Analysis Control Window.

VI. CALCULATIONS

A. Waters

$$\text{Conc Hg, } \mu g/L = \frac{\mu g \text{ of Hg in sample}}{\text{L of sample}}$$

B. Soils

$$\text{Conc Hg mg/kg} = \frac{\mu g \text{ of Hg in sample}}{\text{weight of sample in g}}$$

Note: Samples are to be calculated on a dry weight basis. A separate percent solid's determination is required.

VII. DAILY QUALITY CONTROL

A. ICV/CCV

Immediately after the instrument has been calibrated, the accuracy of the calibration shall be verified . A standard that is from a source other than the calibration standards will be analyzed (ICV). The concentration currently used is 2.0 µg/L. If the deviation exceeds 10% of the true value, the analysis must be terminated, the problem corrected, the instrument recalibrated and the calibration reverified.

The CCV is the same solution as the ICV and is analyzed every 10 analytical samples and at the end of the run. This solution ensures calibration accuracy during the run. If the deviation is greater than 10% from the true value, the analysis must be terminated and the problem corrected. All samples analyzed since the last compliant CCV must be reanalyzed.

B. ICB/CCB

A blank must be run after every ICV and CCV. If the absolute value of the blank exceed the PQL, terminate the analysis and correct the problem. Recalibrate, verify calibration and reanalyze all samples since the last compliant blank.

C. PREPARATION BLANK (PB)

A blank consisting of DI water processed through the sample preparation procedure will be prepared and analyzed with each batch of samples digested or for every 20 samples, whichever is more frequent. If the absolute value of the concentration in the blank is above the PQL, the lowest concentration of that analyte in the associated samples must be 10x the blank concentration. Otherwise, all samples associated having a concentration less than 10x the blank concentration and above the PQL, must be redigested and reanalyzed for that analyte. The sample concentration is not to be corrected for the blank value.

D. MATRIX SPIKE / MATRIX SPIKE DUPLICATE (MS/MSD)

A sample must be spiked in duplicate for each SDG or per 20 samples digested, whichever is more frequent. The Spike must be added before the digestion begins. The sample is spiked so that the final concentration of Hg in solution is 2 µg/L for waters (2ml of 100ppb / 100ml sample) and 1mg/kg for soils (2ml of 100ppb / 0.2g sample). Recovery is calculated as follows:

$$\% \text{ Recovery } * = \frac{(SSR - SR)}{SA} \times 100$$

Where: SSR = Spiked sample result - µg/L or mg/kg
SR = Sample result - µg/L or mg/kg
SA = Spike added - µg/L or mg/kg

* Spike recovery should be between 75%-125%. Calculated RPD on the MS/MSD should be ≤ 20%. If the solid samples fail these criteria, matrix interference will be cited and may be investigated via redigestion. If the aqueous samples fail these criteria then the entire associated SDG will be redigested.

E. ADDITIONAL DUPLICATE SAMPLE ANALYSIS (SD) (not required)

A sample may be prepared and analyzed in duplicate for each SDG or per client request, in addition to the MS/MSD. Calculate the Relative Percent Difference (RPD) as follows:

$$RPD * = \frac{(|S-D|)}{(S+D)/2} \times 100$$

Where: S = Sample result - µg/L or mg/kg
D = Duplicate sample result - µg/L or mg/kg

* Calculated RPD on the aqueous sample duplicates should be ≤ 20% if the sample results are > 10x the MDL. If the samples results are ≤ 10x the MDL the RPD should be ≤ 67% the MDL. If the aqueous samples fail these criteria then the entire associated SDG will be redigested.

F. LABORATORY CONTROL SAMPLE (LCS)

A solid LCS will be analyzed for each SDG or for every 20 soil samples prepared. The LCS is prepared and analyzed using all procedures applied to the samples. If the LCS is not within acceptance criteria provided by the manufacturer, the analysis will be terminated, the problem corrected and the samples associated with the LCS redigested and reanalyzed. An aqueous LCS is not required for Hg.

G. DOCUMENTATION

Instrument Log Books:
Record the applicable information in the designated log book of the instrument being used for the analysis. Information must include deviations, run sequence, maintenance, etc.

Standard Prep Log Book:
Record the necessary information in the prep log book, including source, lot numbers, and volumes and weights utilized.

Control Charts:
The analyst records the percent recovery of the LCS on the appropriate control chart. The purpose of the control chart is identify out-of-control data points and to monitor shifts and/or trends in the analysis performance.

Data Validation:
After analysis, a peer or supervisor review of data will be performed. After this validation, the reviewer shall initial the log books and actual run.

VIII. REFERENCES

Methods 7470A and 7471A, USEPA Test Methods for Evaluating Solid Waste, SW846, Third edition November 1986 and updates.

APPENDIX A - RUN SEQUENCE

CALIBRATION STANDARDS:
STD 0.0 ppb
STD 0.2 ppb
STD 0.5 ppb
STD 1.0 ppb
STD 2.0 ppb
STD 5.0 ppb
STD 10.0 ppb
STD 20.0 ppb

CALIBRATION CHECKS:
ICV 20.0 ppb
ICB 0.0 ppb

SAMPLE RUN SEQUENCE:

1	PB
2	LCS (SOILS)
3	SAMPLE 1
4	SAMPLE 1 SD
5	SAMPLE 1 MS
6	SAMPLE 1 MSD
7	SAMPLE 2
8	SAMPLE 3
9	SAMPLE 4
10	SAMPLE 5
11	CCV
12	CCB
13	SAMPLE 6
14	SAMPLE 7
15	SAMPLE 9
16	SAMPLE 10
17	SAMPLE 11
18	SAMPLE 12
19	SAMPLE 13
20	SAMPLE 14
21	SAMPLE 15
22	SAMPLE 16
23	CCV
24	CCB

TABLE 1

CONCENTRATION OF Hg - PPB	WORKING STANDARD - ml/100 ml
0.2*	0.2
0.5	0.5
1.0	1.0
2.0	2.0
5.0	5.0
10.0	10.0
20.0	20.0
10.0**	10.0**

* Reporting limit.
** ICV - CCV made from a separate 1000 mg/L Hg source.

STANDARD OPERATING PROCEDURE

METALS BY GFAA - SW846

METHOD 7000 SERIES

SOP NUMBER	HO-I-034-B
AUTHOR	DAVID ROSE
EFFECTIVE DATE	MAY 16, 1994

APPROVAL

David Rose 5-23-94
Metals Supervisor Date

Russell Lee Moya 5-23-94
Inorganic Laboratory Manager Date

Kevin Oda 5-23-94
Quality Assurance Officer Date

I. PURPOSE

The purpose of this procedure is to provide a format for the analysis of metals by GFAA under SW846 Method 7000 series.

II. APPLICATION

A. This method applies to drinking, surface, saline waters, domestic and industrial wastes, EP extracts, soils, sludges, sediments, industrial and other solid wastes.

B. SAFETY INFORMATION

Standard laboratory safety practices should be followed.

III. SUMMARY

A predetermined volume of sample is injected into a pyrolytically coated graphite tube inside the furnace unit, then dried, ashed and atomized through a temperature scheme entered into the furnace programmer. At the instant of atomization, the resulting absorption of light will be directly proportional to concentration.

IV. RESPONSIBILITIES

A. QUALITY ASSURANCE OFFICER

1. The Quality Assurance Officer has overall responsibility for monitoring implementation of and adherence to the policies and procedures set forth in this document.

2. The Quality Assurance Officer will conduct semi-annual audits of the facility to monitor adherence to this and other SOPs. The results of the audit will be reported to Regional Management and Corporate Quality.

B. INORGANIC LABORATORY MANAGER/METALS SUPERVISOR

1. The manager/supervisor has responsibility to ensure adherence to this SOP.

2. The manager/supervisor will ensure that this SOP is reviewed on an annual basis.

3. The manager/supervisor will ensure that the Quality Assurance Office is notified when revisions to the SOP are required.

C. ANALYST

1. The analyst is responsible for following all procedures set forth in this document. The analyst will report any deviations to the procedures set forth in this document.

2. The analyst is responsible for reviewing the SOP on an annual basis and reporting any required revisions to the department manager or supervisor.

V. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. At the time of review, any required revisions will be incorporated and the superseded document replaced.

VI. DISTRIBUTION

A. Distribution of this SOP will be determined by the Quality Assurance Office.

B. Distribution records will be maintained by the Quality Assurance Office.

VII. APPARATUS AND CHEMICALS

A. GLASSWARE/HARDWARE

1. Autoanalysis cups

2. Pyrolytically coated graphite furnace tubes and platforms.

3. Volumetric flasks, various sizes, class A.

4. Eppendorf mechanical pipets, various sizes.

5. Zeeman 5100, Zeeman 30/30 instruments.

B. REAGENTS

1. Deionized water. Water should be monitored for impurities (Type II).

2. Concentrated nitric acid, (HNO_3)

3. NIST traceable stock solutions (1000 mg/L) 2 sources of each.

4. Matrix modifiers (refer to Table 1).

VIII. SAMPLE HANDLING/STORAGE

A. SAMPLING PROCEDURE

All sample containers must made of Polyethylene or glass.

B. SAMPLE PRESERVATION

Soil/Sediment samples must be stored at 4°C (±2°C). Store aqueous samples at room temperature preserved to PH < 2 with HNO_3.

C. HOLDING TIME LIMITS

The hold time for metals other than Hg is 180 days.

IX. PROCEDURE

A. Turn on spectrometer, HGA furnace, computer and printer.

B. Turn on cooling water.

C. Turn on Argon gas.

D. Call up appropriate element file from software. For detailed operation instructions refer to instrument manual.

E. Turn on appropriate lamp and let warm up in accordance with manufacturer's instructions.

F. Operating parameters are addressed in appendix 1.

G. Aqueous digestions are addressed in SOP HO-I-031-A.

H. Soil digestions are addressed in SOP HO-I-032-A.

X CALIBRATION

Calibration standards must be prepared fresh daily or each time an analysis is to be made and discarded after use. A blank and three calibration standards must be prepared . Standards should contain similar acid concentrations as the samples to be analyzed (refer to Table 1). An average of 2 readings for each standard is required. A linear correlation coefficient of $\geq$ 0.995 is required.

XI. RUN SEQUENCE (SEE TABLE 2 FOR ORDER)

A. INITIAL CALIBRATION VERIFICATION (ICV) AND CONTINUING CALIBRATION VERIFICATION (CCV)

1. Immediately after the instrument has been calibrated, the accuracy of the calibration shall be verified . A standard will be analyzed that is from a source other than the calibration standards. The concentration should be at or near the midpoint of the calibration curve. When the ICV is outside the acceptance range of 90 to 110% of the true value, the analysis must be terminated, the problem corrected, the instrument recalibrated and the calibration reverified.

2. The CCV is the same solution as the ICV and is analyzed every 10 analytical samples (20 injections). This solution ensures calibration accuracy during the run. If the CCV is outside the acceptance range of 80 to 120% of the true value, the analysis must be stopped and the problem corrected

B. INITIAL CALIBRATION BLANK (ICB) AND CONTINUING CALIBRATION BLANK (CCB)

1. A blank must be run after every ICV and CCV. If the absolute value of the blank exceeds the reporting limit , terminate the analysis, correct the problem, recalibrate, verify calibration and reanalyze all samples since the last compliant blank.

C. PREPARATION BLANK (PB)

A prep blank will be analyzed for each digestion group or for every 20 samples prepared, whichever is more frequent. The prep blank is prepared and analyzed using each procedure applied to the samples. The element of interest cannot be present in the prep blank at or above the reporting limit . Otherwise, redigest and reanalyze all associated samples. If reanalysis is not possible, flag samples to indicate blank contamination.

D. LABORATORY CONTROL SAMPLE (LCS)

An LCS will be analyzed for each digestion group or for every 20 samples prepared. The LCS is prepared and analyzed using each procedure applied to the samples. If the LCS is not within acceptance criteria, the analyses must be terminated, the problem corrected and the samples associated with the LCS redigested and reanalyzed. The control limits are laboratory derived.

E. SPIKE SAMPLE PREPARATION (Sample S)

A sample must be spiked for each digestion group or per 20 samples digested, whichever is more frequent. The Spike must be added before the digestion begins.

The control limits for the spiked sample are 75 to 125%. If the LCS is acceptable and the spiked sample is outside control limits, flag sample as matrix interference. Recovery is calculated as follows:

$$\% \text{ Recovery} = \frac{(SSR - SR)}{SA} X100$$

Where: SSR = Spiked sample result,
SR = Sample result,
SA = Spike added,

F. DUPLICATE SAMPLE ANALYSIS (Sample D)

One sample must be prepared and analyzed in duplicate for each digestion group or for each 20 samples, whichever is more frequent. The acceptable RPDs are as follows: $\leq$ 67% for samples having concentrations $\leq$ 10x MDL and $\leq$ 20% for sample concentrations > 10x MDL. Calculate the Relative Percent Difference (RPD) as follows:

$$RPD = \frac{(|S-D|)}{(S+D)/2} X100$$

Where: S = Sample result,
D = Duplicate sample result,

If the RPD values are outside the acceptance limits, flag the associated data.

G. ANALYITCAL FURNACE SPIKES (P)

When using furnace techniques, each matrix must be examined for interference effects (e.g., samples exhibiting MS recoveries outside of control limits) by use of a furnace spike (aslo known as a post-digestion spike) or serial dilution. This should be done for each sample matrix analyzed by GFAA. The recoveries should be between 85 to 115% to denote absence of matrix effects. Agreement of results (within 10%) for the serial dilution indicates the absence of interference. If outside control limits successively dilute and reanalyze, matrix modification or MSA should be used.

H. METHOD OF STANDARD ADDITIONS (MSA)

Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addtion may be used.

XII. DOCUMENTATION

1. Instrument Log Books

Record the applicable information in the designated log book of the instrument being used for the analysis. Information must include program deviations, run sequence, maintenance, etc.

2. Standard Prep Log Book

Record the necessary information in the prep log book, including source, lot numbers, and volumes utilized.

3. Control Charts

Plot the % recovery of the LCS on the appropriate control chart. If an out-of-contol situation exists , record the corresponding nonconformance - corrective action number on the control chart.

4. Data Review

After analysis, a peer or supervisor review of data will be performed. The reviewer shall initial the log books and actual run.

5. Reporting Units

Aqueous samples are reported in ug/L. Solid samples are reported in mg/Kg based on wet weight.

XIII.REFERENCES

a. USEPA Test Method for Evaluating Solid Waste, SW846 third edition, November 1986.

b. Zeeman 5100, Zeeman 30/30 Instrument manuals .

APPENDIX 1
OPERATING PERAMETERS

ELEMENT	λ	SLIT	PLATFORM/ WALL	CHAR TEMP °C	ATOMIZE TEMP °C
As	193.7	0.7	P	1300	2300
Be	234.9	0.7	P	1500	2500
Cd	228.8	0.7	P	900	1600
Co	242.5	0.2	P	1400	2500
Cr	357.9	0.7	P	1600	2500
Mo	313.3	0.7	W	1800	2650
Pb	283.3	0.7	P	900	1700
Sb	217.6	0.7	P	1000	2300
Se	196.0	0.7	P	900	2100
Tl	276.8	0.7	P	800	1500
V	318.4	0.7	W	1100	2600

STEP 1	DRY TEMP.	The sample/std dries on the platform/tube without splattering. Generally at ≅ 60 s. at 110° C.
STEP 2	CHAR	The temperature gets hot enough to burn off interferences without losing particular analyte. Generally about 30 s.
STEP 3	ATOMIZE	The analyte is atomized and absoption is measured. Generally about 4 s.
STEP 4	BURN OFF	The tube/platform is cleaned of any carry- over at ≅2700°C for 4 s.
STEP 5	COOL DOWN	The tube/platform is cooled down for the next sample/standard.

NOTE: Program is used as a quide only. Temperatures may vary depending on nature of tube, samples etc.

TABLE 1

ELEMENT	MATRIX MODIFIER	CALIBRATION STANDARDS µg/L			ICV-CCV µg/L	REPORTING LIMIT µg/L
As	1	20.0	30.0	50.0	25.0	3.0
Be	2	1.0	2.0	3.0	2.0	0.5
Cd	3	1.0	2.0	3.0	2.0	0.5
Co	2	20.0	30.0	50.0	25.0	1.0
Cr	2	10.0	20.0	30.0	20.0	1.0
Mo	NONE	2.0	3.0	5.0	2.5	0.5
Pb	3	20.0	30.0	50.0	25.0	2.0
Sb	4	20.0	30.0	50.0	25.0	3.0
Se	4	20.0	30.0	50.0	25.0	3.0
Tl	5	20.0	30.0	50.0	25.0	1.0
V	2	10.0	20.0	30.0	20.0	4.0

MATRIX MODIFIERS

1) 9.8g $Ni(NO_3)_2 \cdot 6H_2O$ into 500mL deionized water.

2) 1.7g $Mg(NO_3)_2 \cdot 6H_2O$ into 100mL deionized water.

3) 5.5g $(NH_4)_2HPO_4$ + 0.07g $Mg(NO_3)$ into 100mL deionized water.

4) 20.0g $Ni(NO_3)_2 \cdot 6H2O$ + 8.8g $Mg(NO_3)_2 \cdot 6H_2O$ into 100 mL deionized water.

5) 1mL H_2SO_4 into 100mL deionized water.

TABLE 2
RUN SEQUENCE

CALIBRATION	
1	ICV
2	ICB
3	PB
4	LCS
5	SAMPLE 1
6	SAMPLE 1P
7	SAMPLE 1D
8	SAMPLE 1S
9	SAMPLE 2
10	SAMPLE 3
11	SAMPLE 4
12	SAMPLE 5
13	CCV
14	CCB
15	SAMPLE 6
16	SAMPLE 7
17	SAMPLE 8
18	SAMPLE 9
19	SAMPLE 10
20	SAMPLE 11
21	SAMPLE 12
22	SAMPLE 13
23	SAMPLE 14
24	SAMPLE 15
25	CCV
26	CCB

PACE ANALYTICAL SERVICES, INCORPORATED
HOUSTON LABORATORY

STANDARD OPERATING PROCEDURE

Analysis of Soil and Aqueous Sample Extracts for organochlorine pesticides/PCB's

SOP NUMBER	HO-O-010-D
AUTHOR	Matt Hearne
Effective Date	September 4, 1996
Supersedes	HO-O-010-C

APPROVAL

Department Supervisor — 9/4/96 Date

Quality Assurance Officer — 9-5-96 Date

TABLE OF CONTENTS

Analysis of Soil and Aqueous Sample Extracts for organochlorine pesticides/PCB's

I. Purpose and Applicability

This method is used to determine the concentration of various organochlorine pesticides and polychlorinated biphenyls (PCBs) using specifications from SW-846 Method 8081. Table 1 indicates compounds that may be determined by this method.

II. Summary of Method

This method provides gas chromatographic conditions for detection of ppb levels of certain organochlorine pesticides and PCBs. Both neat and diluted organic liquids may be analyzed by direct injection. A 0.5 to 2.0ul sample is injected into the gas chromatograph, and compounds in the GC effluent are detected by electron capture detector (ECD).

The sensitivity of this Method usually depends on the level of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, this method may also be performed on samples that have undergone cleanup.

III. Interferences

Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large late-eluting peaks, especially in the 15% and 50% fractions from the Florisil cleanup. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

Elemental sulfur is encountered in many sediment samples, marine algae, and some industrial wastes. The solubility of sulfur is similar to the organochlorine pesticides and will be evident in the GC chromatograms using the electron capture detectors. Refer to the SOP HO-O-013 - "Extraction of Pesticide/PCBs in Solids by Method 3550A" for instructions on sulfur removal.

IV. Safety

This procedure requires the use of materials, which when handled improperly, pose potential health risk to everyone in the laboratory. It is important that all necessary safety precautions are followed. This includes the use of properly operating fume hoods, appropriate gloves, protective eyewear, lab coats, and respiratory protection as necessary. Users of this procedure must be cognizant of inherent syringe hazards, proper disposal procedures for contaminated materials, and appropriate segregation of waste. Everyone involved in the procedure must be familiar with the MSDS for solvents and chemicals used. Any additional information can be received by consulting with your Chemical Hygiene Plan.

V. Responsibility

A. Personnel

1. All personnel involved with sample preparation and analysis are responsible for adherence to this Standard Operating Procedure (SOP).

2. Personnel are responsible for ensuring that any deviations to this SOP are reported.

3. All personnel are responsible for notifying the department manager/supervisor of any required revisions to the SOP.

B. Department manager/supervisor

1. The department manager/supervisor is responsible for ensuring adherence to this SOP.

2. The department manager/supervisor is responsible for performing an annual review of the SOP and reporting any required revisions to the Quality Assurance Office.

C. Quality assurance office (QAO)

1. The QAO is responsible for conducting periodic laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Regional Management and Corporate Quality.

2. The QAO is responsible for ensuring that all revisions to the SOP are implemented.

3. The QAO is responsible for determining distribution of and maintaining document control for this SOP.

VI. Reviews/revisions

A. This SOP will be reviewed on an annual basis at a minimum.

B. At the time of review, any required revisions will be incorporated.

C. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

VII. Distribution

This SOP will be issued to the GC lab and any other areas deemed appropriate by the QAO.

VIII. Equipment and Supplies

A. Gas Chromatographs:
Varian 3400 GC, HP 5890 GC or equivalent

B. Columns:
Rtx-5 0.32mm x 30M film thickness of 1.0um
Rtx-35 0.32mm x 30M film thickness of 1.0um
or equivalents

C. Detectors:
Dual Electron capture (ECD) for each instrument

D. Carrier gas:
Helium. Carrier flow is approximately 5mls/min. Make-up flow (use zero Nitrogen)is approximately 20-30mls/min.

E. Solvents:
Hexane and Acetone (pesticide quality or equivalent)

IX. Standards

Sources: Restek, Supelco, Protocol, Chem Service or equivalents

Stock standards are purchased from a commercial supplier in two separate mixes. The mixes with their list of analytes and concentration are in the table below:

Pest mix A:	conc. (ug/ml)
alpha-BHC	2000
Heptachlor	2000
Gamma-BHC(Lindane)	2000
Endosulfan I	2000
Dieldrin	2000
Endrin	2000
p,p'-DDD	2000
p,p'-DDT	2000
Methoxychlor	2000

Pest mix B:	conc. (ug/ml)
beta-BHC	2000
delta-BHC	2000
Aldrin	2000
Heptachlor Epoxide	2000
Chlordane (alpha)	2000
Chlordane (gamma)	2000
p,p'-DDE	2000
Endosulfan Sulfate	2000
Endrin Aldehyde	2000
Endrin Ketone	2000
Endosulfan II	2000

Multiresponse standards (individual):	
Toxaphene	200
Technical Chlordane	200
PCBs	1000

Appendix IX standards (individual):	
Chlorobenzilate	100
Diallate	100
Isodrin	100
Kepone	1000

Surrogates:	
2,4,5,6-TCMX and DCBP	200

X. Calibration Standards

Calibration Standards are made from dilutions of the stock standards above and combined to form one calibration mix. The multiresponders are made from dilutions of stock standards and are injected separately. The Appendix IX standards are purchased as separate solutions and combined at the appropriate concentrations into one mixture. The dilutions made should bracket the working range of the instrument.
All standard mixes are made up in Hexane and stored in the refrigerator and kept only 6 months or whenever the calibration standard shows signs of degradation.

XI. Calibration

The external standard calibration procedure is used. Each analyte of interest, except multiresponders, is run at a minimum of 5 different concentrations, a calibration curve is constructed and the %RSD for each component are calculated and must not exceed 20%. The concentration of the calibration standards should define the working range of the specific instrument.
See Figure 1 for an example of a typical calibration sequence including concentrations for an HP 5890-II GC. See Figures 1a-1d for retention time orders and example chromatograms for primary and secondary columns. See Figure 2 for an example of a typical calibration sequence including concentrations for a Varian 3400 GC. See Figures 2a-2f for retention time orders and example chromatograms for primary and secondary columns.

The Appendix IX standards (Chlorobenzilate, Isodrin, Kepone, and Diallate) are prepared together as a separate standard mixture with each at their own appropriate concentration. This standard mix is analyzed under its own 5-pt calibration.

For multiresponding components (i.e. toxaphene, tech-chlordane, and PCBs) a single injection at a mid-concentration level is made before sample analysis. For screening purposes the identification of the multiresponder is made by pattern recognition (direct visual comparison to the standard). If the patterns indicate a match, a positive hit is concluded and the appropriate single point standard equal or close to the concentration of the analyte detected is injected and the 5 major peaks are selected for quantitation.

Continuing calibrations must be verified every 10 samples and the %RPD for each analyte of interest must not exceed 15%. A midpoint concentration of all analytes of interest must be included. For sample analyses that require PCBs, a mixture of Aroclor 1016/1260 may be used. If any analyte of interest fails the criteria, then all samples analyzed after the last passing calibration must be reanalyzed.

DDT and endrin are easily degraded in the injection port if the injection port or the front of the column is dirty. This is the result of buildup of high boiling residue from sample injection. Check for degradation problems by injecting a Performance Evaluation Mixture each day or at the beginning of each 12 hour shift. If degradation of either DDT or endrin exceeds 15%, take corrective action before proceeding with calibration, by cleaning the GC injection port. Calculate percent breakdown as follows:

$$\%\ \text{breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation Peak area (DDE + DDD)}}{\text{Total DDT peak area (DDT + DDE + DDD)}} * 100$$

$$\%\ \text{breakdown for Endrin} = \frac{\text{Total endrin degradation peak area (E.A. + E.K.)}}{\text{Total endrin peak area (E. + E.A. + E.K.)}} * 100$$

Where: E.A. = Endrin Aldehyde
E.K. = Endrin Ketone
E. = Endrin

XII. Retention Time Windows

Whenever a new column is installed into the GC, retention time windows must be established. The windows are initially established by monitoring and recording the rention times of the peaks for the single responding compounds, and one representative peak for the multiresponding compounds. The data are collected from three separate injections of standards over a 72 hour period of time. The retention time window is calculated as plus or minus three times the standard deviation of the retention time for each peak. For multiresponders, the analyst should rely mainly on pattern recognition. For compounds that have standard deviations of retention time that are extremely small, the retention time window from a compound that it is close to, and similar with, should be substituted.

For daily analysis, the absolute retention time from the standards run within that 12 hour period of time will be used as the midpoint of the window. Tentative identification of target compounds will be based on peaks that elute during the daily retention time window.

XIII. Analytical Sequence

Table 3 shows a typical sequence of analysis beginning with an initial calibration, sample analyses, and continuing calibration, and closing calibration.

See Figure 3 for a listing of routine reporting limits for each analyte in aqueous samples assuming a 1000 ml aliqout and a 10 ml final volume. Reporting limits for soil samples will be proportionately higher as the extraction volume will dictate. Elevated reporting limits due to interferences from sample matrices may be improved by following sample cleanup procedures.

XIV. Quality Control

A. Surrogates Recoveries

Calculate the surrogate recoveries for all the samples, blanks, LCS's, and matrix spikes. The recoveries should fall within the acceptance limits established by historical data. The control limits are defined as the mean plus or minus three times the standard deviation of the recovery for each surrogate collected over a period of time.
If the recoveries of both surrogates fall outside the control limits, check the instrument performance and/or reanalyze the samples in question. If the surrogate recoveries are still out of control, then re-extract the samples which were out of the surrogate control limits.

B. Method Blanks

A method blank is prepared and analyzed with every batch of up to 20 samples extracted. If any target compounds are detected in the method blank at or above the reporting limit, all samples with positive hits for those compounds must be re-extracted.

C. LCS Recoveries

A Lab Control Sample (LCS) prepared from a source separate from the calibration standards is run with every batch of up to 20 samples extracted. The LCS control limits are calculated from historical data. If the LCS results are outside the control limits, corrective action must be taken. The analyst should first check the instrument performance, followed by reanalysis of the LCS and possibly re-extraction of all samples associated with it.

D. MS/MSDs

A matrix spike and matrix spike duplicate are extracted at a 5% frequency or as specified by the project. If the recovery of any compound spiked does not fall within the control limits established for

the LCS, that compound must demonstrate acceptable recovery in the associated LCS, and the data flagged as indicative of possible matrix interference.

IX. Applicable Documents/References

Test Methods for Evaluating Solid Waste Physical/Chemical Methods, US EPA SW 846, 3rd edition: Method 8081A.

TABLE I

Spike Solution Concentration Levels
(mg/L)

Pesticides	Level
alpha-BHC	1.0
beta-BHC	1.0
delta-BHC	1.0
gamma-BHC (Lindane)	1.0
Heptachlor	1.0
Aldrin	1.0
Heptachlor Epoxide	1.0
Endosulfan I	1.0
Dieldrin	1.0
4,4'-DDE	1.0
Endrin	1.0
Endosulfan II	1.0
4,4'-DDD	1.0
Endrin Aldehyde	1.0
4,4'-DDT	1.0
Endrin Ketone	1.0
Methoxychlor	1.0
Chlorobenzilate	10
Diallate	10
Isodrin	1.0
Kepone	10

TABLE II

Solution Concentration Levels
for
Multiresponse Analytes
(mg/L)

Pesticides	Level
Aroclor 1242	10
Toxaphene	5
Chlordane	5

TABLE III

Calibration and Analytical Sequence

Performance Evaluation Mix (PEM)
Toxaphene (low level)
Technical Chlordane (low level)
PCB 1016/1260 (low level)
PCB 1221 (low level)
PCB 1232 (low level)
PCB 1242 (low level)
PCB 1248 (low level)
PCB 1254 (low level)
Hexane
Pesticide Std. (level #1)
Pesticide Std. (level #2)
Pesticide Std. (level #3)
Pesticide Std. (level #4)
Pesticide Std. (level #5)
Hexane
Appendix IX Std. (level #1)
Appendix IX Std. (level #2)
Appendix IX Std. (level #3)
Appendix IX Std. (level #4)
Appendix IX Std. (level #5)
Hexane
Method Blank (if applicable)
LCS (if applicable)
Sample
.
.
Sample (10 total)
Pesticide Std. (mid-pt calibration level)
Instrument Blank
Sample
.
.
Sample (10 total)
Pesticide Std. (mid-pt calibration level)

Note: Method Blanks, LCS's, MS/MSD's are included in the total of 10 samples between calibration checks; instrument blanks are not. Calibration check standards must be analyzed at a minimum every 12 hours of sample analysis.

Aug 96 10:52 AM page 1
quence: C:\HPCHEM\1\SEQUENCE\081996.SEQ

erator: 41038 WZ

quence preparation date: 20 Aug 96 10:52 AM

ta File Names: Auto

ta File Subdirectory: 081996

rt of methods to run: full method

a barcode mismatch: inject anyway

mment:
Standard Ref. H064-94-109-3 Method: 8081 Dual capilary column

Sample Log Table

q. Line	Vial Num.	Sample Name	Sample Multiplier Amount	ISTD Amount	Cal. Line	Method Name	Ini/ Vial
ONT							
1							
AR							
1	1	pe				PF081996	1
1	2	1016/1260 .2/.1				PF081996	1
1	3	1221/1254 .2/.1				PF081996	1
1	4	1232 std 100ppb				PF081996	1
1	5	1242 std 100ppb				PF081996	1
1	6	1248 std 100ppb				PF081996	1
1	7	tox std 500ppb				PF081996	1
1	8	chld std 100ppb				PF081996	1
1	9	pest std ppb 5				PF081996	1
1	10	pest std ppb 200				PF081996	1
1	11	pest std ppb 100				PF081996	1
1	12	pest std ppb 300				PF081996	1
1	13	pest std ppb 400				PF081996	1
1	14	h373574 blk				PF081996	1
1	15	h373573 lcs				PF081996	1
1	16	h433330				PF081996	1
1	17	h433330 ms				PF081996	1
1	18	h433330 msd				PF081996	1
1	19	h433332				PF081996	1
1	20	h433333				PF081996	1
1	21	h433334				PF081996	1
1	22	h433335				PF081996	1
1	23	h372726 blk				PF081996	1
1	24	h372725 lcs				PF081996	1
1	25	h432655				PF081996	1
1	26	pest chk 200				PF081996	1

Figure 1
Calibration Sequence for HP 5890-II

Figure 1a

External Standard Report

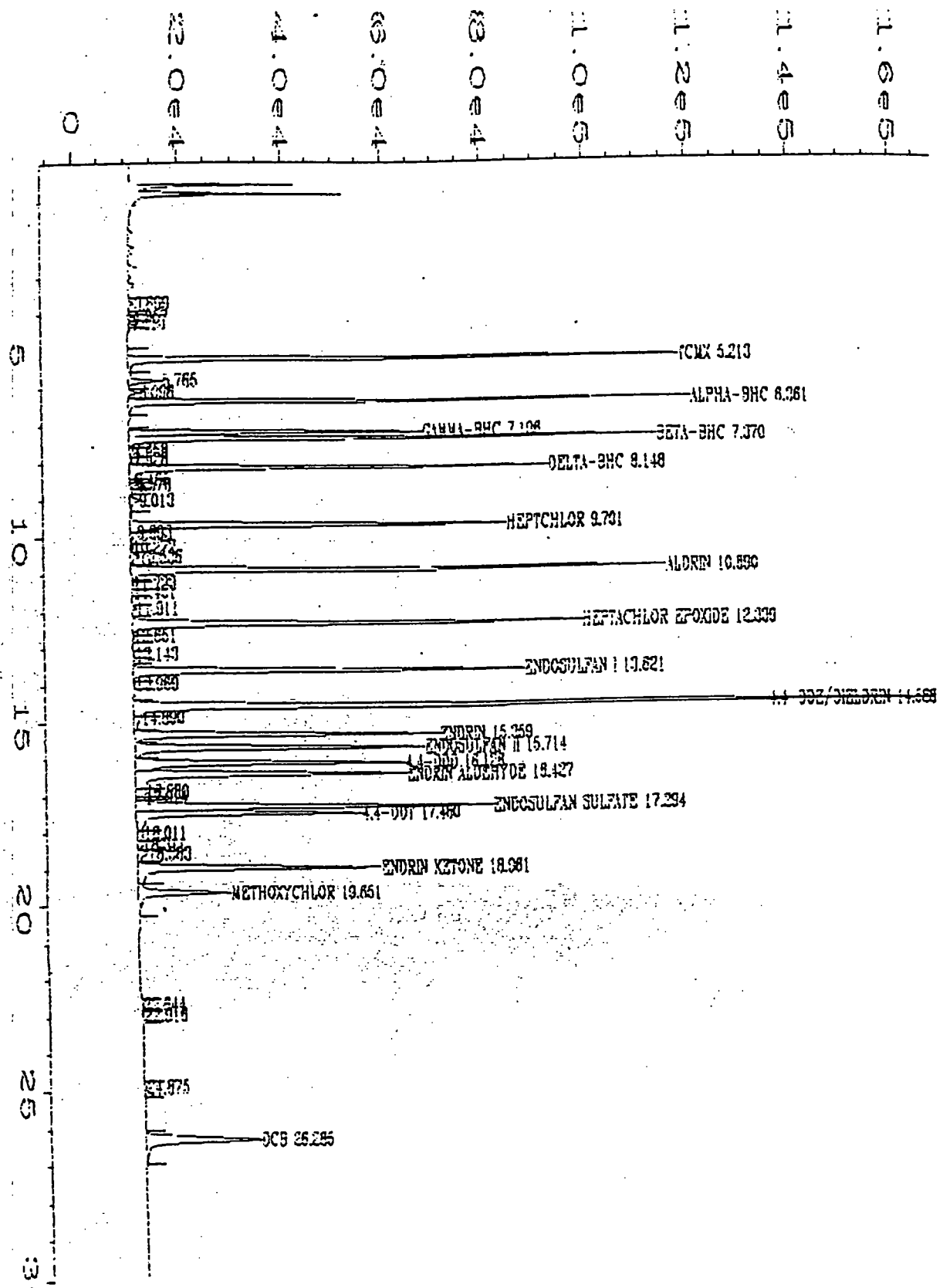
ata File Name : C:\HPCHEM\1\DATA\081996\011F0101.D
perator : 41038 WZ
nstrument : 5693GC
ample Name : pest std ppb 200
in Time Bar Code:
equired on : 19 Aug 96 08:18 PM
eport Created on: 20 Aug 96 11:04 AM
ast Recalib on : 20 AUG 96 10:26 AM
ultiplier : 1

Page Number : 1
Vial Number : 11
Injection Number : 1
Sequence Line : 1
Instrument Method: PF081996.MTH
Analysis Method : PF081996.MTH
Sample Amount : 0
ISTD Amount :

ig. 1 in C:\HPCHEM\1\DATA\081996\011F0101.D

et Time	Area	Type	Width	Ref#	ug/l	Name
5.213	476889	BV	0.068	1	100.00	TCMX
6.361	507553	VV	0.072	1	100.000	ALPHA-BHC
7.196	284974	BV	0.078	1	100.00	GAMMA-BHC
7.370	509948	VV	0.077	1	100.00	BETA-BHC
8.148	427556	VV	0.081	1	100.000	DELTA-BHC
9.701	433363	VV	0.091	1	100.000	HEPTCHLOR
10.890	622169	VV	0.092	1	100.00	ALDRIN
12.339	538993	PV	0.095	1	100.00	HEPTACHLOR EPOXIDE
13.621	483776	VV	0.098	1	100.000	ENDOSULFAN I
14.588	1019295	PV	0.101	1	200.000	4.4-DDE/DIELDRIN
15.359	380638	VV	0.100	1	100.00	ENDRIN
15.714	378444	VV	0.105	1	100.00	ENDOSULFAN II
16.126	353366	VV	0.104	1	100.00	4.4-DDD
16.427	394097	VV	0.114	1	100.000	ENDRIN ALDEHYDE
17.294	474391	VV	0.105	1	100.000	ENDOSULFAN SULFATE
17.480	321088	VV	0.111	1	100.000	4.4-DDT
18.961	344790	VV	0.113	1	100.00	ENDRIN KETONE
19.651	143771	VV	0.125	1	100.000	METHOXYCHLOR
26.285	226061	PV	0.161	1	100.00	DCB

Figure 1b



Data File Name : C:\HPCHEM\1\DATA\081996\011F0101.D
Operator : 41038 WZ
Instrument : 5693GC
Sample Name : best std ppb 200
Run Time Bar Code:
Acquired on : 19 Aug 96 08:18 PM
Report Created on: 20 Aug 96 11:04 AM
Last Recalib on : 20 AUG 96 10:26 AM

Page Number : 1
Vial Number : 11
Injection Number : 1
Sequence Line : 1
Instrument Method: PF081996.MTH
Analysis Method : PF081996.MTH
Sample Amount : 0
ISTD Amount :

Figure 1c

External Standard Report

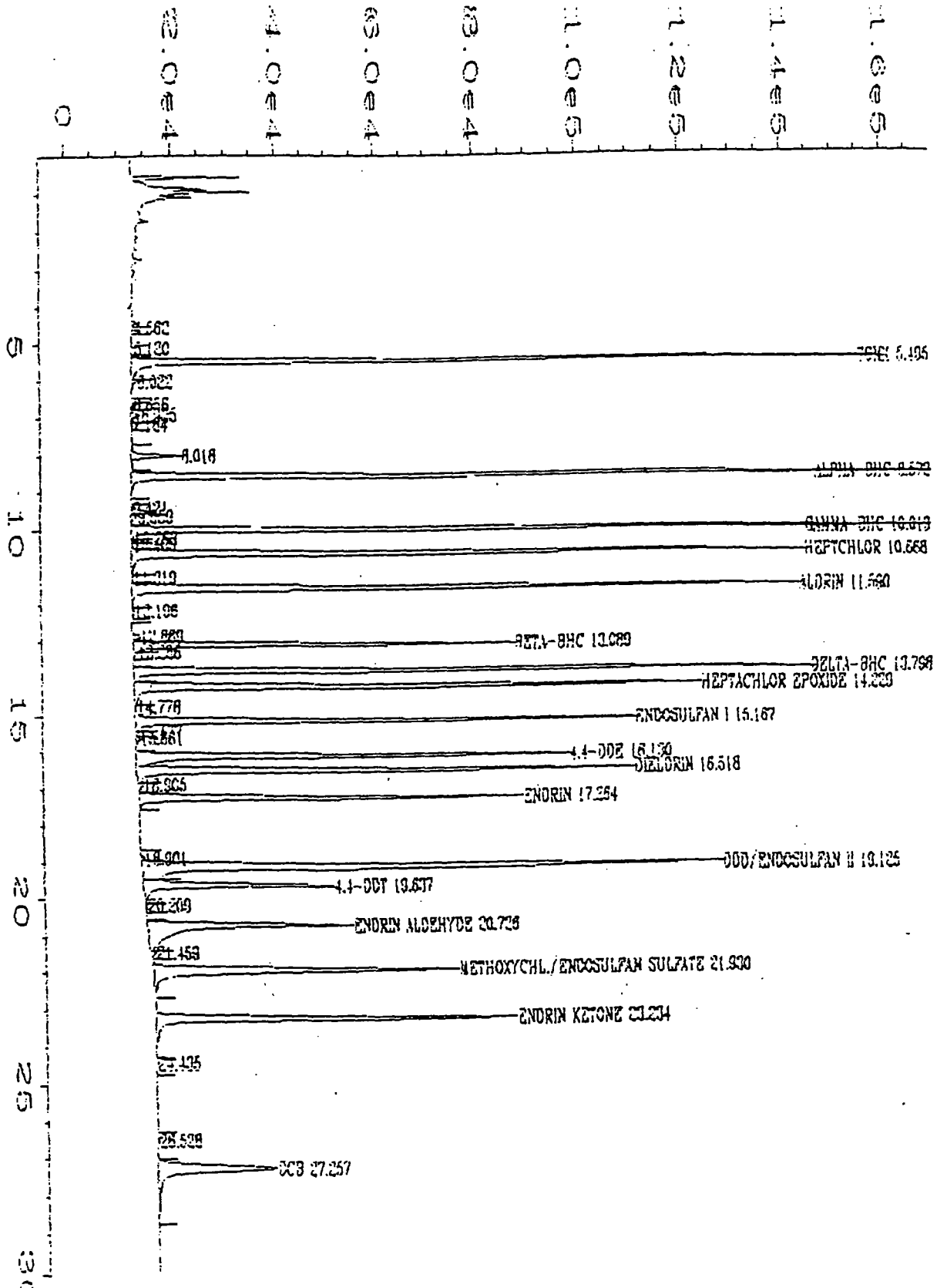
ta File Name : C:\HPCHEM\1\DATA\081996\011R0101.D
erator : 41038 WZ
strument : 5693GC
mple Name : pest std ppb 200
n Time Bar Code:
quired on : 19 Aug 96 08:18 PM
port Created on: 20 Aug 96 11:04 AM
st Recalib on : 20 AUG 96 10:38 AM
ltiplier : 1

Page Number : 1
Vial Number : 11
Injection Number : 1
Sequence Line : 1
Instrument Method: PF081996.MTH
Analysis Method : PR081996.MTH
Sample Amount : 0
ISTD Amount :

g. 2 in C:\HPCHEM\1\DATA\081996\011R0101.D

t Time	Area	Type	Width	Ref#	ng/ml	Name
5.495	747384	VV	0.078	1	100.00	TCMX
8.572	981501	BB	0.083	1	100.00	ALPHA-BHC
10.019	873701	PV	0.086	1	100.000	GAMMA-BHC
10.668	803871	VV	0.096	1	100.00	HEPTCHLOR
11.590	794868	VV	0.096	1	100.000	ALDRIN
13.089	431093	VV	0.090	1	100.000	BETA-BHC
13.798	743315	PV	0.088	1	100.000	DELTA-BHC
14.229	707078	VV	0.100	1	100.000	HEPTACHLOR EPOXIDE
15.167	634086	VV	0.101	1	100.000	ENDOSULFAN I
16.130	557487	PV	0.101	1	100.000	4.4-DDE
16.518	622258	VV	0.100	1	100.000	DIELDRIN
17.264	470658	VV	0.098	1	100.000	ENDRIN
19.125	907117	VV	0.125	1	200.000	DDD/ENDOSULFAN II
19.637	273631	VV	0.110	1	100.000	4.4-DDT
20.726	387491	PB	0.139	1	100.00	ENDRIN ALDEHYDE
21.930	526303	BB	0.126	1	200.000	METHOXYCHL./ENDOSULFAN SULFATE
23.234	492437	BB	0.106	1	100.000	ENDRIN KETONE
27.257	289648	BB	0.190	1	100.000	DCB

Figure 1d



Data File Name	: C:\HPCHEM\1\DATA\081996\011R0101.D	Page Number	: 1
Operator	: 410BB WE	Vial Number	: 11
Instrument	: 5890SC	Injection Number	: 1
Sample Name	: best std ppb 200	Sequence Line	: 1
Run Time Bar Code:		Instrument Method:	PB081996.MTH
Acquired on	: 19 Aug 96 08:19 PM	Analysis Method	: PB081996.MTH
Report Created on:	20 Aug 96 11:05 AM	Sample Amount	: 0
Last Recalib on	: 20 AUG 96 10:38 AM	ISTD Amount	:

Sequence File : D:\2700\DATA1\09PEST\81D2996.seq
Created by : 07694 DFF on : 4/29/1996 10:21 AM
Edited by : 07694 DFF on : 4/30/1996 11:34 AM
Number Of Times Edited : 8

Sequence File Header Information:
Study Name :
Segment Interface : NO
Number of Cycles : 74
Instrument Type : 760 / 900 Series Intelligent Interface
Injection Type : SINGLE

Sequence Sample Descriptions

Cycle	Sample Name	Sample Number	Site	Rack	Vial	Sample Amount	ISTD Amount	Inj. Volume	Dil. Factor	Mult	Divisor	Addend	Inst File	Output Device
1	Hexane		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
2	PEM		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
3	Hexane		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
4	1016/1260 1 ppm		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
5	1221/1254 1 ppm		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
6	1232 1 ppm		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
7	1242 1 ppm		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
8	1248 1 ppm		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
9	Hexane		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
10	Tox 500 ppb		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
11	Tech Chlor 100 ppb		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
12	Hexane		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
13	8080 5 ppb		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
14	8080 25 ppb		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
15	8080 50 ppb		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
16	8080 75 ppb		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
17	8080 100 ppb		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
18	Hexane		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
19	Hexane		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
20	H367463-W Blk		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
21	H367462-W LCS		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
22	H367463-W Blk/MS		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
23	H367463-W Blk/MSD		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
24	Hexane		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
25	H424648-W		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
26	H424649-W		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
27	H424650-WS1		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
28	H424651-WS1		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
29	H424652-WS1		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
30	H424653-WS1		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
31	H424663-W		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
32	H424664-WS1		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
33	H424665-W		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
34	Hexane		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
35	Hexane		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
36	8080 50 ppb		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
37	Hexane		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
38	H424643-W		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
39	H424647-W		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
40	H424655-W		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
41	H424658-W		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:
42	H424641-W		A	1	1	1.000	1.000	1.000	1.000	1.000	1.000	0.000	81D2996F	LPT1:

Figure 2
Calibration Sequence for Varian 3400

Figure 2a

```
Software Version: 3.2 <16C20>
Sample Name   : 8080 50 ppb                Time          : 4/30/1996  07:46 AM
Sample Number:                             Study         :
Operator      : 07694 DFF

Instrument    : 3852GC                     Channel : A      A/D mV Range : 10000
AutoSampler   : NONE
Rack/Vial     : 0/0

Interface Serial # : 9198571160   Data Acquisition Time: 4/29/1996  07:14 PM
Delay Time    : 0.00   min.
End Time      : 31.29  min.
Sampling Rate : 2.9412   pts/sec

Raw Data File  : d:\2700\data1\09pest\81D2996\A094015.raw
Result File    : d:\2700\data1\09pest\81D2996\A094015.rst
Instrument File: C:\2700\DATA1\09PEST\81D2996F.ins
Process File   : C:\2700\DATA1\09PEST\81D2996F.prc
Sample File    : C:\2700\DATA1\09PEST\81D2996F.smp
Sequence File  : d:\2700\data1\09pest\81d2996.seq

Inj. Volume    : 1 NG/UL                    Area Reject      : 500.00
Sample Amount  : 1.0000                     Dilution Factor  : 1.00
```

8080 Pesticides Reported in ng/ml

3852GC Detector A - Rtx 5

Group Report For : SURROGATE

Time [min]	Area [uV*sec]	BL	Adjusted Amount	Component Name
4.965	14470817.00	BV	100.7956	Tetrachloro-M-Xylene
29.473	10588014.00	BB	99.6660	Decachlorobiphenyl
	25058832.00		200.4616	

Group Report For : 8080 PEST

Time [min]	Area [uV*sec]	BL	Adjusted Amount	Component Name
6.104	15772736.00	BB	50.4999	alpha-BHC
6.976	4142977.50	BV	48.9286	beta-BHC
7.146	14751850.00	VB	50.1176	gamma-BHC
7.988	13617794.00	VE	50.9671	delta-BHC
9.668	14221429.00	BB	50.0138	Heptachlor
10.999	15592825.00	VV	50.4723	Aldrin
12.701	13454865.00	BV	49.8207	Heptachlor Epoxide
14.209	12567437.00	BB	49.4802	Endosulfan I
15.362	12757959.00	VV	49.6284	Dieldrin
15.502	12855187.00	VE	50.6746	p,p'-DDE
16.289	8770177.00	VB	49.3053	Endrin

Figure 2b

17.376	8458052.00	BV	49.8336	p,p'-DDD
17.631	7292702.00	VE	49.9894	Endrin Aldehyde
18.706	7611347.50	BV	49.5785	Endosulfan Sulfate
19.047	8758344.00	VB	49.7877	p,p'-DDT
20.731	9843130.00	BB	49.7950	Endrin Ketone
21.871	3715490.00	BB	51.1444	Methoxychlor
	1.93e8		899.5634	

END

Report Stored in ASCII File: d:\2700\data1\09pest\81D2996\A094015.TX0

Figure 2c

Chromatogram

Sample Name : 8080 50 ppb
FileName : d:\2700\data1\09pest\81D2996\A094015.raw
Method : 81D2996F.ins
Start Time : 0.00 min End Time : 31.29 min
Scale Factor: 0 Plot Offset: 0 mV

Sample #: Page 1 of 1
Date : 4/30/1996 07:46 AM
Time of Injection: 4/29/1996 07:14 PM
Low Point : 0.00 mV High Point : 2000.00 mV
Plot Scale: 2000 mV

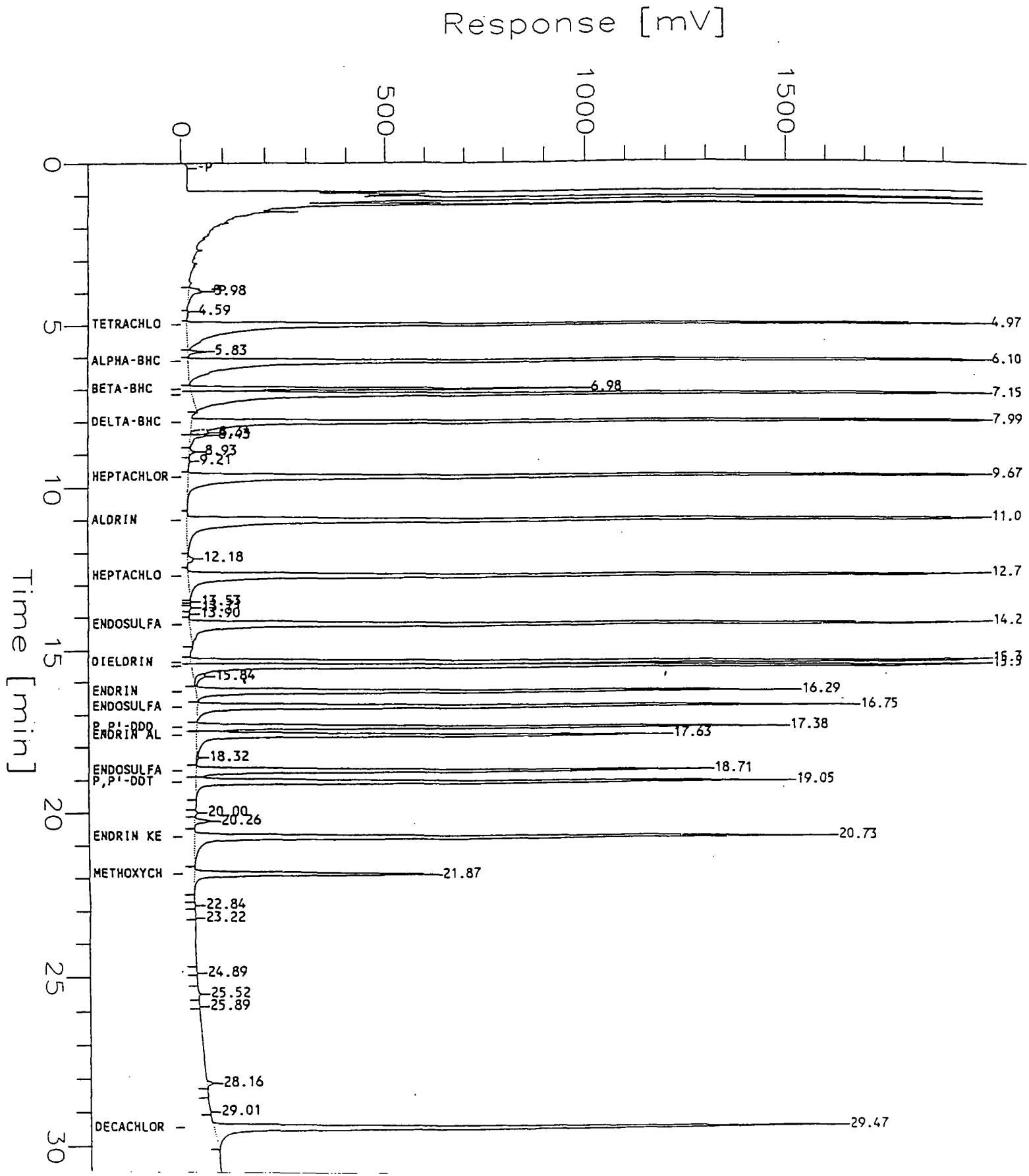


Figure 2d

```
Software Version: 3.2 <16C20>
Sample Name   : 8080 50 ppb                Time          : 4/30/1996  07:47 AM
Sample Number:                             Study         :
Operator      : 07694 DFF

Instrument    : 3852GC                     Channel : B     A/D mV Range : 10000
AutoSampler   : NONE
Rack/Vial     : 0/0

Interface Serial # : 9198571160   Data Acquisition Time: 4/29/1996  07:14 PM
Delay Time      : 0.00   min.
End Time        : 31.29  min.
Sampling Rate   : 2.9412   pts/sec

Raw Data File   : d:\2700\data1\09pest\81D2996\B094015.raw
Result File     : d:\2700\data1\09pest\81D2996\B094015.rst
Instrument File: C:\2700\DATA1\09PEST\81D2996F.ins
Process File    : C:\2700\DATA1\09PEST\81D2996R.prc
Sample File     : C:\2700\DATA1\09PEST\81D2996R.smp
Sequence File   : d:\2700\data1\09pest\81d2996.seq

Inj. Volume     : 1 NG/UL                  Area Reject       : 500.00
Sample Amount   : 1.0000                   Dilution Factor   : 1.00
```

8080 Pesticides Reported in ng/ml

3852GC Detector B - Rtx 1701

Group Report For : *SURROGATE*

Time [min]	Area [uV*sec]	BL	Adjusted Amount	Component Name
4.715	12136992.00	BE	107.0952	Tetrachloro-M-Xylene
29.008	7901831.00	BB	98.8718	Decachlorobiphenyl
	20038824.00		205.9670	

Group Report For : 8080 PEST

Time [min]	Area [uV*sec]	BL	Adjusted Amount	Component Name
7.673	12858452.00	BB	52.4174	alpha-BHC
9.197	11616857.00	BB	51.2646	gamma-BHC
9.834	11826795.00	BB	51.0117	Heptachlor
10.814	11874404.00	BB	50.5384	Aldrin
12.788	3849788.75	BB	48.9465	beta-BHC
13.524	11441799.00	VV	50.7100	delta-BHC
13.900	10457135.00	BB	49.8215	Heptachlor Epoxide
14.957	9727135.00	BB	49.7132	Endosulfan I
16.299	9483380.00	BV	49.6294	p,p'-DDE
16.594	10605622.00	BB	49.9735	Dieldrin
17.471	7092935.00	BB	49.8509	Endrin
[illegible]	7681202.00	BV	50.0162	Endosulfan II

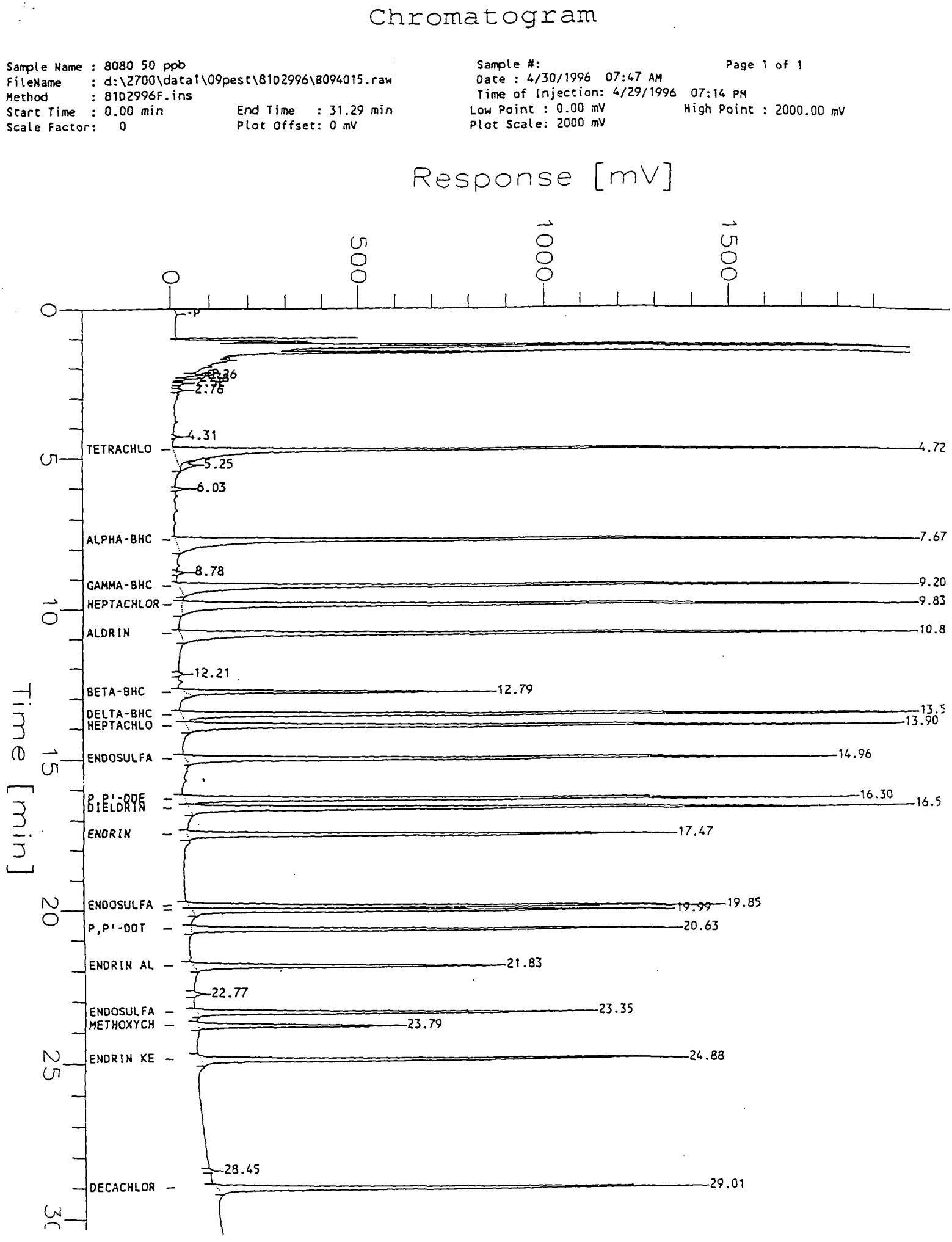
Figure 2e

19.993	7004482.00	BB	50.1136	p,p'-DDD
20.626	7079967.50	BB	50.1937	p,p'-DDT
21.832	4889122.50	BB	50.3779	Endrin Aldehyde
23.354	5859994.50	BB	49.8273	Endosulfan Sulfate
23.787	3014186.00	BB	50.9428	Methoxychlor
24.877	7285776.00	BB	50.1430	Endrin Ketone
	1.53e8		905.4915	

END

Report Stored in ASCII File: d:\2700\data1\09pest\81D2996\B094015.TX0

Figure 2f


Chromatogram
Sample Name : 8080 50 ppb
FileName : d:\2700\data1\09pest\8102996\8094015.raw
Method : 81D2996F.ins
Start Time : 0.00 min
End Time : 31.29 min
Scale Factor: 0
Plot Offset: 0 mV
Sample #:
Page 1 of 1
Date : 4/30/1996 07:47 AM
Time of Injection: 4/29/1996 07:14 PM
Low Point : 0.00 mV
High Point : 2000.00 mV
Plot Scale: 2000 mV
Response [mV]
0
500
1000
1500
Time [min]
0
5
10
15
20
25
30
TETRACHLO
ALPHA-BHC
GAMMA-BHC
HEPTACHLOR
ALDRIN
BETA-BHC
DELTA-BHC
HEPTACHLO
ENDOSULFA
P,P'-DDE
DIELDRIN
ENDRIN
ENDOSULFA
P,P'-DDT
ENDRIN AL
ENDOSULFA
METHOXYCH
ENDRIN KE
DECACHLOR
2.76
4.31
4.72
5.25
6.03
7.67
8.78
9.20
9.83
10.8
12.21
12.79
13.5
13.90
14.96
16.30
16.5
17.47
19.85
20.63
21.83
22.77
23.35
23.79
24.88
28.45
29.01

Software Version: 3.2 <16C20>
Sample Name : A IX 50 ppb
Sample Number:
Operator : 07694 DFF

Time : 9/5/1996 08:20 AM
Study :

Instrument : 3852GC
AutoSampler : NONE
Rack/Vial : 0/0

Channel : A A/D mV Range : 10000

Interface Serial # : 9198571160 Data Acquisition Time: 9/3/1996 12:14 PM
Delay Time : 0.00 min.
End Time : 31.29 min.
Sampling Rate : 2.9412 pts/sec

Raw Data File : D:\2700\DATA1\09PEST\AIXI0396\A099002.RAW
Result File : C:\temp\~rst2E21.rst
Instrument File: C:\2700\DATA1\09PEST\IXI0396A.ins
Process File : C:\2700\DATA1\09PEST\IXI0396A.prc
Sample File : C:\2700\DATA1\09PEST\IXI0396A.smp
Sequence File : <none>

Inj. Volume : 1 NG/UL
Sample Amount : 1.0000

Area Reject : 500.00
Dilution Factor : 1.00

3852GC Detector A - Rtx 1701
Reported in ng/ml

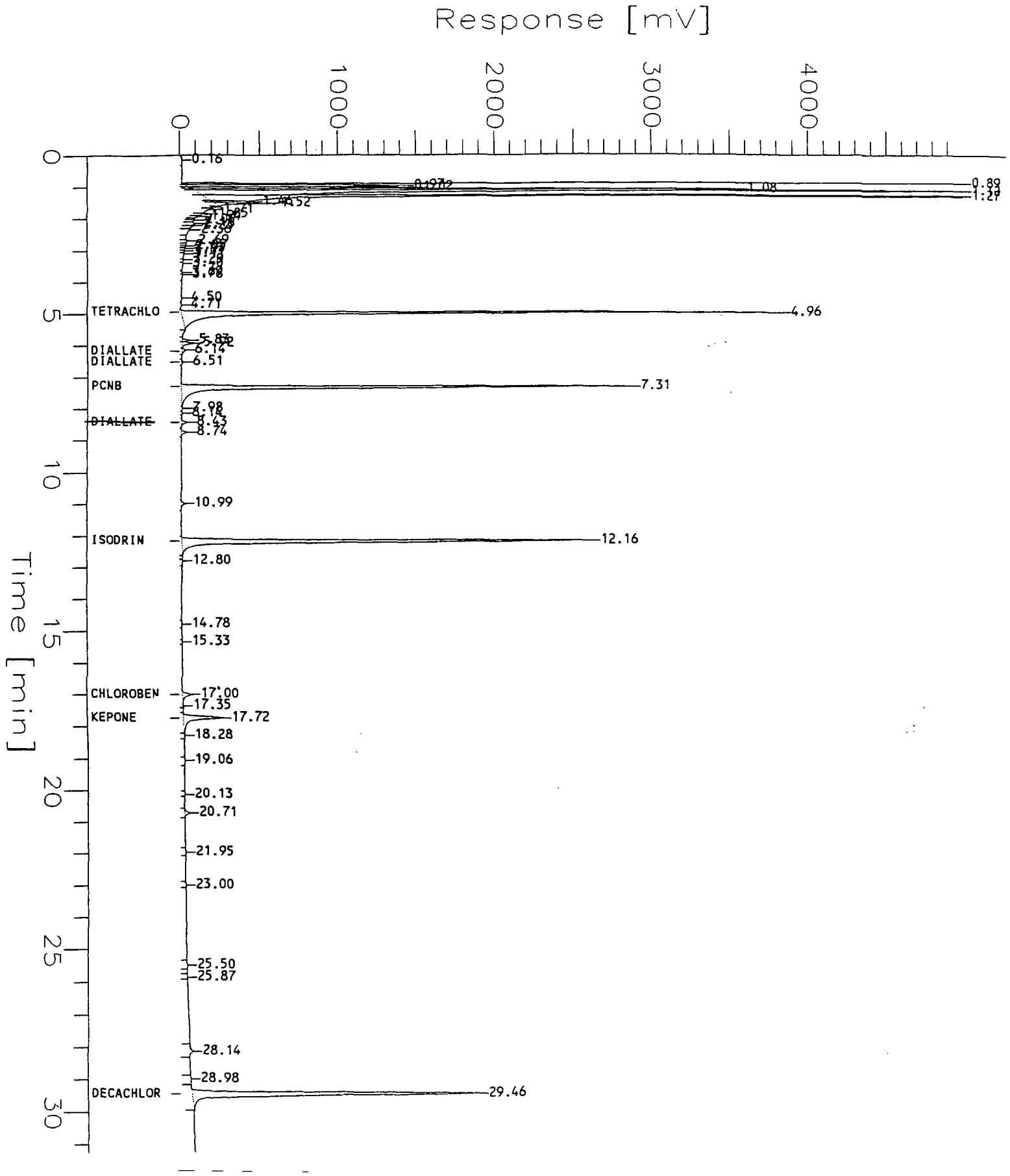
Time [min]	Area [uV*sec]	BL	Adjusted Amount	Component Name
4.961	15618015.00	BB	50.0001	Tetrachlorl-m-Xylene
6.135	121105.59	VB	50.0023	Diallate #1
6.511	45475.15	BB	49.9727	Diallate #2
7.305	13256692.00	BV	50.0004	PCNB
8.427	~~151061.69~~	BB	~~49.9873~~	~~Diallate #3~~
12.158	14369631.00	BB	50.0001	Isodrin
17.004	387466.63	BE	49.9957	Chlorobenzilate
17.715	1904696.75	BV	49.9999	Kepone
29.455	12298219.00	BB	100.0002	DECACHLOROBIPHENYL
	58152364.00		499.9586	

END

Chromatogram

Sample Name : A IX 50 ppb
FileName : D:\2700\DATA1\09PEST\AIXI0396\A099002.RAW
Method : IXI0396A.ins
Start Time : 0.00 min End Time : 31.29 min
Scale Factor: 0 Plot Offset: 0 mV

Sample #:
Date : 9/5/1996 08:21 AM
Time of Injection: 9/3/1996 12:14 PM
Low Point : 0.00 mV High Point : 5000.00 mV
Plot Scale: 5000 mV



LIMS Information ps2 372658 (V5.0) h08294 12:21 Mon 19-Aug-96

Batch	Sample	Type	Test	C	A#	Ref	Anlt	Result	RPD/%R	Unit	Book	Page
65508	H372658	BLNK	G120WR	L	1		4,4' DDD	< 0.05		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		4,4' DDE	< 0.05		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		4,4' DDT	< 0.05		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		Aldrin	< 0.05		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		Chlordane	< 1		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		Dieldrin	< 0.05		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		Endosulfan I	< 0.05		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		Endosulfan II	< 0.05		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		Endosulfan sulfate	< 0.05		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		Endrin	< 0.05		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		Endrin aldehyde	< 0.05		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		Heptachlor	< 0.05		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		Heptachlor epoxide	< 0.05		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		Methoxychlor	< 0.05		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		PCB-1016	< 1		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		PCB-1221	< 1		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		PCB-1232	< 1		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		PCB-1242	< 1		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		PCB-1248	< 1		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		PCB-1254	< 1		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		PCB-1260	< 1		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		Toxaphene	< 5		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		alpha-BHC	< 0.05		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		beta-BHC	< 0.05		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		delta-BHC	< 0.05		ug/L	H063-94	150
65508	H372658	BLNK	G120WR	L	1		gamma-BHC	< 0.05		ug/L	H063-94	150
65508	H372658	SURR	$PSTW	L	2	1	Decachlorobiphenyl		70		H063-94	150
65508	H372658	SURR	$PSTW	L	2	1	Tetrachloro-m-xylene		68		H063-94	150

28 rows selected.

Figure 3
Reporting Limits for Aqueous Samples

STANDARD OPERATING PROCEDURE

Total Dissolved Solids

SOP Number	HO-I-020-A
Author	Bruce Brown
Effective Date	January 14, 1997
Supersedes	First Issue

Approvals:

Bruce Brown 1/23/97

General Chemistry Supervisor Date

1/23/97

Quality Assurance Officer Date

I. PURPOSE

The purpose of this Standard Operation Procedure (SOP) is to establish a uniform procedure for filterable residue.

II. SCOPE/APPLICATION

A. Summary of Method

This SOP is applicable to drinking, surface and saline waters, domestic and industrial wastes.

B. Test Concentrations

Range 10 mg/L to 20,000 mg/L

C. Interferences

1. Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hydroscopic and will require prolonged drying, desiccation and rapid weighing.

2. Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to ensure that all the bicarbonate is converted to carbonate.

3. Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.

D. Safety Information

Each chemical compound used in this SOP should be treated as a potential health hazard. Care should be used while handling samples because of toxicity. Exposure to these substances must be reduced to the lowest possible level by whatever means available (i.e., gloves, lab coats, eye protection, fume hoods). Reference files of OSHA regulations and Material Safety Data Sheets (MSDSs) are available to all personnel involved in this analysis.

III. RESPONSIBILITIES

A. Quality Assurance Officer

1. The Quality Assurance Officer (QAO) has overall responsibility for ensuring that this SOP is implemented and followed.

2. The QAO is responsible for conducting semi-annual laboratory audits to monitor adherence to this and other SOPs. Results of the audits will be reported to Regional Management and Corporate Quality.

3. The QAO is responsible for ensuring that all revisions to the SOP are implemented.

4. The QAO is responsible for determining distribution of and maintaining document control for this SOP.

B. Laboratory Management

1. The department supervisors and managers are responsible for ensuring that this SOP is understood, implemented, and adhered to by all designated personnel.

2. The department supervisor/manager is responsible for performing and annual review of this SOP and reporting and required revisions to the Quality Assurance Department.

C. Analyst

The analysts are responsible for adhering to this SOP, analyzing replicate standards, and reporting results in a timely manner.

D. Reviews/Revisions

1. This SOP will be reviewed on an annual basis at a minimum.

2. Required revisions will be incorporated at time of review.

3. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

E. Distribution

Distribution of this SOP will be determined by the QAO.

IV. APPARATUS AND MATERIALS

A. Glassware / Hardware

1. Glass fiber filter, 4.7 cm without organic binder
2. Filter holder membrane filter funnel
3. Suction flask, 500 mL
4. Vacuum pump
5. Beakers, 200 mL
6. Desiccator
7. Drying oven, 180°C
8. Analytical balance, capable of weighing to 0.0001 g

B. Procedure

1. Prepare Evaporating Dishes

   a. Heat clean dishes at 178-182°C for 1 hour (minimum).

      Note: If volatile dissolved solids will also be run, heat the clean dishes in a muffle furnace maintained at 550°C ± 50°C for 1 hour (minimum). Allow the dishes to cool partially in air to near room temperature before desiccating.

   b. Transfer dishes into a desiccator. Store there until needed.

   c. Weigh each dish immediately before using. Record the dish identification and tare weight in the analysis log.

2. Prepare Glass-Fiber Filters

   a. Insert a glass-fiber filter, wrinkled side up, into the filtration apparatus.

   b. Apply vacuum and wash the filter with three successive 20 mL volume of reagent water. Continue suction to remove all traces of water.

   c. Assemble the filtering apparatus and begin suction. Wet the filter with a small volume of reagent water to seat it.

   d. Mix the sample well by shaking.

   e. Immediately measure out 100 mL of sample into a graduated cylinder.

   f. Quantitatively transfer the sample to a preweighed dish. Rinse the graduated cylinder with a small volume of reagent water three times to effect the quantitative transfer.

   g. Rinse the glass-fiber filter with filtering apparatus with three successive 10 mL volumes of reagent water, allowing complete drainage between rinsings.

   h. Continue suction to remove all traces of water form the filter.

   i. Quantitatively transfer filtrate to a preweighed evaporating dish. Rinse the flask with small volumes of reagent water three times to effect the quantitative transfer.

   j. Transfer the dish to a 103-105°C oven and evaporate the sample to dryness.

   k. Transfer the dish to an oven maintained at 178-182°C. Dry the sample for 1 hour (minimum).

   l. Remove the dish from the oven and allow it to cool to room temperature in a desiccator.

   m. Weigh the dish. Record the weight in the analysis log.

n. Repeat steps k through m until the constant weight is obtained. Constant weight is weight loss between two consecutive weighings is <4% or <0.0005 g., whichever is less.

C. Calculation

$$\frac{A - B \times 1000}{C} = mg/L$$

Where:

A= Final weight of dish + residue in g
B= Initial weight of dish in g
C= Initial volume in L

D. Quality Control

1. Method Preparation Blank (PB)
A method blank must be analyzed with each batch of 20 samples. It is processed in the same manner as the samples using 100 mL of DI water.

2. Duplicate Sample (D)

a. Duplicate sample analysis will be performed at a frequency of one in every 10 samples if sufficient volume of sample is provided.

b. The relative percent difference (RPD) is calculated as:

$$\mathbf{RPD=} \quad \frac{(|S-D|)\,(100)}{(S + D)\,/2}$$

Where:

S = Sample value, mg/L
D= Duplicate sample value, mg/L

D. Reference

EPA Methods for the Chemical Analysis of Water and Waste, March 1983, Method 160.1

STANDARD OPERATING PROCEDURE

Analysis of Volatile Organic Compounds - Method 8260A

SOP NUMBER	HO-O-019-B
AUTHOR	Mark Hackfeld
EFFECTIVE DATE	August 28, 1996
SUPERSEDES	HO-O-019-A

APPROVAL

[signature] 8-30-96

GC/MS Supervisor — Date

[signature] 8-30-96

Quality Assurance Officer — Date

I. PURPOSE and APPLICABILITY

Method 8260A is a GC/MS method applicable to analysis of volatile organic compounds using specifications from SW-846 Method 8260A. While volatility is defined as the tendency of a substance or material to pass into the vapor state at a given temperature, the procedures employed in method 8260A analyses allows a more general interpretation.

For our purposes at the Pace-Houston lab, any compound which can be successfully purged from a water-based solution or slurry, trapped (absorbed) and concentrated and then (desorbed) injected into a gas chromatographic column in an amount sufficient to allow quantification (e.g. 2 1/2 ratio of signal to noise) is a volatile organic compound (VOC). This purging technique may be done at ambient temperature or as high as 60 Deg C, utilizing Helium as a carrier gas.

Method 8260A is applicable to a large number of original sample matrices-ground water, sludges caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter caps, spent carbons, catalysts, soils, sediments. Solids with organic absorbant characteristics (incinerator) ash, activated carbon) must first be extracted with methanol and then diluted into water. This procedure will automatically result in a dilution factor of 125%. Some samples with high organic content must also be first diluted into methanol and then subsequently be added to water.

See the attached Table 1 for the VOCS that are currently contained in Pace's instrument library and have been demonstrated to be guantifiable by this technique.

II. SUMMARY OF METHOD

Some type of sample (solution, emulsion, mixture, or slurry) is placed in an appropriate purging chamber. Helium is passed through the sample in the form of finely divided bubbles. The VOC enriched helium is then passed thru a thin metal tube containing Tenax, silica gel and activated coconut charcoal in equal portions and then vented to the atmosphere. This 3-phase "trap" will efficiently desorb organic compounds. After purging for 11 minutes with a flow of 30-40 mL/ minutes of helium. The GC oven is cooled to 40 Degrees Centigrade and the trap is flash-heated to 180 Degree Centigrade and backflushed with Helium onto the column. After the desorption step, the GC oven containing the column is then ramped to a maximum temperature using Helium as a carrier gas. This

effects an efficient separation of even the most closely related organic compounds (e.g. as trans-alkenes or meta, or ortho aromatic isomers).

The capillary column is interfaced to a Finnigan Mass spectrometer (Incos 50 series) via a heated glass jet separator, which removes most of the carrier gas or to an HP 5972 MSD via capillary direct.

Within the evacuated ion source, the VOA molecules are bombarded by high energy electrons (70eV) producing a fingerprint pattern of charged particles unique to each compound. The charged particles are separated by amount of mass by alternately varying applied radio frequency energy and electrical energy on the length of four evenly spaced rods (called quadrupoles). Positively charged particles are collected and processed into a narrow time dependent stream by the application of electrical potential across a series of lenses. The signals produced when these particles strike a charged plate are amplified and counted by the SuperIncos data system or HPchem station. Positive qualification depends on matching known ion spectra and appropriate compound retention time. Quantification is achieved by comparing the area of EPA mandated base peak with the area of the base peak from an internal standard and a known amount of the analyte (calibration standard).

III. INTERFERENCES

This technique is sensitive enough and complicated enough that lab contamination can become a major problem. The three compounds most frequently present as lab contamination are methylene chloride, 2-butanone (MEK) and acetone.

Methylene chloride easily becomes airborne and bleeds through the teflon septa of samples and purging chamber valves. 2-butanone is a common contaminant of methanol, the universal solvent for VOA's. The only brand of methanol shown to be contaminant free is Burdick & Jackson Purge and Trap grade methanol. Acetone may be residual from glassware cleaning.

Sometimes residual amounts of a standard on a syringe will contaminate the internal standard/surrogate (IS/SS) mix and thereby be introduced into every sample. Internal standard contamination is easily monitored by first analyzing a method blank which is DI water with IS/SS added. Contaminated IS/SS mixes must be disposed of properly. If the IS/SS mix is not the source, and the 5 mL Leuerlock syringe and valve have been eliminated, the source of contamination is usually the purge chamber and/or purge lines. Previous samples containing VOC's may have contaminated the system. Step the automated liquid sampler

to a clean purge vessel (check the log book Versus chromatograms for last sample purged from that vessel). Purge DI H20 from the clean chamber and check for contamination. If the contaminants are still present serious system contamination may have occurred.

A. Bake out the trap at a higher temperature (220 Degree Centigrade instead of 180).

B. Turn off the filament and electron multiplier and bake out the column at 225 Degree Centigrade.

C. Fastidiously rinse all syringes and purge chambers with freshly opened methanol.

D. Purge another uncontaminated DI water sample and analyze.

E. If contamination is still present, then disconnect the trap and backflush methanol through the top of the trap connection to the purge vessel.

IV. SAFETY

Safety concerns fall into three categories:

- Exposure to toxic organic chemicals
- Implosion of equipment under high vacuum.
- Injuries from sharp syringes or burns from hot surfaces.

A. ORGANIC EXPOSURE

The health hazard with the most likelihood of occurring is exposure to methanol. methanol is the solvent used for all reagents. It is used to rinse all glassware and syringes. It may be used to dilute and extract samples.

methanol is readily absorbed through the skin. Vinyl gloves must be worn at all times when handling samples, standards or reagents. Normal lab hygiene also requires a lab coat and safety glasses. It is important that the chemist avoid all skin and eye contact with methanol. Avoid breathing the vapors. It is not possible to limit all uses of methanol to the hood, but whenever possible, this should be done.

The working chemist will be required to use a wide variety of toxic organic chemicals to successfully analyze samples. Most often potential

exposure to known toxins occurs during instrument calibration. Fortunately, very small quantities are involved--200 ppb x 0.005L = 1 ug of specific toxin potential exposure resulting from the high END calibration. However, it is important that vinyl gloves be worn at all times, since the solvent-- methanol- could carry dissolved toxins through the skin. These are volatile organics, so it is important that only gas-tight syringes and leuer-lock syringes with gas tight valves be employed.

The biggest risk for exposure to toxic reagents comes during preparation of concentrated (primary stock) standards. Great care must be taken to prevent skin exposure to 20,000 ug/L toxic concentration in methanol. The chemist must also guard against used pump oil. It is considered a very toxic substance. See the maintenance manual for proper procedures when changing pump oil. One must also guard against accidentally injecting himself with standards and samples. All standards must be prepared in a hood.

2. DANGERS FROM HIGH VACUUM EQUIPMENT

Mass spectrometers operate under vacuums in the 10-7 torr range. These are very high vacuums that produce a great deal of stress on relatively fragile equipment. Great care must always be physically exercised when moving about the operating system. Don't bump hot glass surfaces.

The most dangerous part of the volatile Mass Spectrometer is the jet separator. It is very fragile, very hot (>200 Degree Centigrade) and under high vacuum. It frequently becomes clogged and must be removed for cleaning. If not properly aligned when being re-evacuated it will implode. It may also implode if struck with a wrench or if a drop of methanol gets on it. Beware when leak checking any part of the transfer oven.

3. INJURIES/BURNS

The method requires frequent use of syringes. If care is not exercised at all times, a puncture wound may result. The chemist may even inadvertently inject himself with toxins.

The entire GC/MS system may hold the potential for burning a careless analyst. Samples may be heated during the purge. The trap heats up to 180 Degree Centigrade during desorb and bake-out. The GC oven is routinely programmed to 150 Degree Centigrade. The transfer oven and jet separator are kept at 230 DegC. Manifold temperatures are kept at

100 Degree Centigrade. The analyst must keep an awareness of all of these area and wear leather gloves or thermal mittens when necessary. Since liquid nitrogen is used to cool the GC, at times the analyst must guard against frostbite. Wear leather gloves when changing liquid N2 tanks

GENERAL SAFETY REVIEW

Lab coats and safety glasses must be worn at all times. Vinyl gloves must be worn whenever handling samples or reagents. Use a safety hood whenever possible when preparing standards and samples. Be aware of implosion hazards especially the jet separator--be certain it is installed straight and the lid to the transfer oven is on before re-evacuating. Be aware of hot surfaces.

V. RESPONSIBILITY

A. Personnel

1. All personnel involved with sample preparation and analysis are responsible for adherence to this Standard Operating Procedure (SOP).

2. Personnel are responsible for ensuring that any deviations to this SOP are reported.

3. All personnel are responsible for notifying the department manager/supervisor of any required revisions to the SOP.

B. Department Manager/Supervisor

1. The department manager/supervisor is responsible for ensuring adherence to this SOP.

2. The department manager/supervisor is responsible for performing an annual review of the SOP and reporting any required revisions to the Quality Assurance Office.

C. Quality Assurance Officer (QAO)

1. The QAO is responsible for conducting periodic laboratory audits to monitor adherence to this and other SOPs.

Results of the audit will be reported to the Reqional Management and Corporate Quality.

2. The QAO is responsible for ensuring that all revisions to the SOP are implemented.

3. The QAO is responsible for determining distribution of and maintaining document control for this SOP.

VI. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. At the time of review, any required revisions will be incorporated.

C. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

VII. DISTRIBUTION

This SOP will be issued to the GC/MS lab and any other areas deemed appropriately Regional QAO.

VIII. SAMPLE COLLECTION, PRESERVATION, CONTAINERS, AND HOLDING TIME

Samples are delivered to the GC/MS lab by the Sample Custodian. They must be immediately stored in the sample storage refrigerator (4 DegC) and never placed in the refrigerator containing standards.

The holding time for all VOC samples is 14 days from the date of collection. Samples are preserved with HCl at the time of collection and have a holding time of 14 days. Do not accept samples that are not in the proper VOA bottle or with headspace, or VOC samples which have not been kept stored at 4 Degree Centigrade. Check with your supervisor. Every sample should consist of two or more containers that are preserved. Soil samples that are received will be sub-sampled if any other analytical test, digestion or extraction is to be done on the sample. These sub-sampled soils are for the use of the GC/MS volatile lab only. Soil samples must be stored at 4 Degrees Centigrade in a sealed container.

TCLP samples will be delivered to the waste lab personnel. Waste lab personnel must log these samples into the sample log book. These samples must be immediately refrigerated.

IX. Equipment and Supplies

A. Gas Chromatographs and MSD's

- 2 HP 5890 Series II gas chromatograph interfaced to a 5972 MSD which have a Tekmar 2016 connected to a Tekmar ALS 3000 concentrator
- 1 HP 5890 gas chromatograph interfaced to a 5971 MSD which has a Tekmar 2016 connected to a ALS 2000
- 1 Varian gas chromatograph interfaced to a FinniganMat Incos MS which has a Dynatech Dynatrap

B Columns

- HP 90m x 0.32mm id with a 1.8 u film thickness
- Restek 60m x 0.53 mm id with a 2.0 u film thickness

C. Carrier gas - Ultra high purity helium

D. Solvents - Burdick & Jackson purge and trap quality methanol

E. Syringes - 10 ul, 25 ul, 50 ul, and 100 ul Hamilton gas tight syringes. 5mL and 20mL Hamilton glass sample syringe w/Leuer Lock tips. 20 mL plastic syringe for spent sample remove.

F. Analytical balance capable of weighing to the nearest 0.1 gram with calibration weights of 1.0, 5.0, 100.0 grams

X. Standards

Sources: Restek, Supelco, Protocol or equivalents

Stock standards are purchased from a commercial supplier in mixes. The mixes with their list of analytes and concentration are on Table 2. Calibration standards are made up in methanol and stored in the refrigerator and kept only 6 months. If

the calibration standard shows signs of degradation before the 6 month period is up, they are disposed of properly.

XII. Tuning

Every 12 hours of operation the chemist is required to analyze 50 ng of BFB and verify that the ion ratio limits fall within EPA prescribed limits.

XIII. Calibration

Calibration standards are made from dilutions of the stock standards are combined in a 5 mL syringe to make up calibration levels of 20,40,60,80,100ppb and may also include 150 or 200 ppb standard for 5 mL purge or combined in a 20 mL syringe to make up calibration levels of 5,10,20,30,40ppb for 20 mL purge.

Prior to the analysis of samples, the % RSD of the response factors for Calibration Check compounds (CCC'S) for a five-point initial calibration must not exceed 30%. The response factor for System Performance Check Compounds (SPCCS) must be greater than 0.1. The compounds 1,1,2,2-Tetrachloroethane and chlorobenzene must be greater than 0.30.

It is recommended that the RPD for any compound not exceed 30% This is not a requirement and is not always achievable. Consult your supervisor in the event this occurs. You may not analyze samples if the PD on a target analyte exceeds 50% without approval from your supervisor, a QA/QC officer or the lab director.

Method 8260A requires that a calibration check be performed every 12 hours of operation. Certain criteria must be met before additional analysis of samples can proceed. The response factors for Calibration Check compounds (CCC'S) must be compared to an average response factor from a five-point initial calibration, and the percent (PD) difference must not exceed 20%. The response factor for System Performance Check Compounds (SPCCS) must be greater than 0.1. The compounds 1,1,2,2-Tetrachloroethane and chlorobenzene must be greater than 0.30.

Individual areas of the four internal standards in each sample must not vary from the last daily calibration check by more than minus 50% or plus 100% (a factor of 2). Retention times for internal standards in the daily calibration check

standard must not vary more than 30 seconds from the previous daily calibration check standard standard retention times.

If after completing the continuing calibration check, any of the required parameters are not met, do not analyze samples. Do not start a new initial calibration. Do not re-run the continuing calibration. Consult the trouble shooting, preventive maintenance manual or speak with your supervisor.

XIV. Analytical Sequence

A. BFB tune
B. Initial Calibration or Continuing calibration
C. Laboratory Control Sample or LCS
D Blank
E. Samples (5% MS/MSD)

XV. Quality Control

A The GC/MS system must be tuned to meet the BFB specifications set forth in the method for each 12 hours.

B. There must be an initial calibration of the GC/MS system and the GC/MS system must meet the SPCC criteria and the CCC criteria set forth in the method for each 12 hours.

C. An second-source LCS is run in every 12 hour calibration period. If the LCS recoveries are not 75-125%, corrective action must be taken. The analyst should first check the instrument performance, followed by re-analysis of the LCS and re-analysis of all samples if needed.

D. A Blank is run in every 12 hour calibration period. The blank must have target analytes less than the practical quantitation limit (PQL) prior to the analysis of any samples. The surrogate recoveries in the blank must pass acceptance limits.

E. Samples

1. Sample preparation of water samples

a. All samples as well as standard solutions must be allowed to warm to ambient temperature before analysis. Remove the

plunger from a 5-mL syringe and pour in the ambient temperature water sample to just short of overflowing. Replace the syringe plunger and compress the sample venting any residual air while adjusting the sample volume to 5.0 mL. Add 2.5 uL of the IS/SS spiking solution to the 5 mL sample through the opening in the 5 mL syringe barrel. Immediately inject the 5 mL sample into the tekmar purging vessel. Set up the proper method and sequence file through HPChem and analyze the sample.

b. If lower detection limits are required a 20mL sample can be purged instead using a 25 mL syringe and 2 uL of the IS/SS spiking solution. The 20 mL samples should be heated using the tekmar heating jackets which are set to heat the samples to 40 degrees Centigrade. Sample heating insures better recovery of poorly purgeable compounds.

2. Sample preparation of low-level soil samples

a. Prior to weighing out samples, the analytical balance must be checked for accuracy everyday by weighing the calibration weights (1.0, 5.0, 100.0 grams) on the stand. Record to the nearest 0.1 gram the weight of each of the calibration weights in the soil weight logbook. Soil samples must be weighed out on the top loading analytical balance to the nearest 0.1 gram and the weight recorded in the soil weight log book. The soil samples are weighed inside the purge vessel and are weighed by difference. Weigh the purge vessel first. Record this weight to the nearest 0.1 gram. Add soil to the purge tube using a clean spatula until the desired weight is achieved. 5.0 g of soil is the nominal sample weight; lesser sample weights, down to 1.0 g may be used if the sample is known to contain high levels of target compounds. Record this weight to the nearest 0.1 gram as well as the difference which will be the final weight of the soil sample. Immediately take the purge vessel to the ALS 2016 and insert and tighten making sure there is a firm seal with no leaks.

b. Internal standards and surrogate standards must be added using 5 mLs of DI organic-free reagent water. Remove the plunger from a 5-mL syringe and pour in the ambient temperature water to just short of overflowing. Replace the

syringe plunger and compress the water venting any residual air while adjusting the sample volume to 5.0 mL. Add 2.5 uL of the IS/SS spiking solution to the 5 mL sample through the opening in the 5 mL syringe barrel. Immediately inject the 5 mL sample into the tekmar purging vessel which has the soil sample. Set up the proper method and sequence file through HPChem and analyze the sample.

3. Sample preparation of medium-level soil samples

Weigh 4.0 g sample into a tared 20 mL vial. Add 10 mL methanol, cap, and shake for two minutes. Remove the plunger from a 5 mL syringe and and fill until overflowing with organic-free reagent water. Replace the syringe plunger and compress the water, venting any residual air, while adjusting the sample volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of sample extract and IS/SS spiking solution. Add 2.5 µL IS/SS spiking solution and 100 µL methanol extract from the sample. Proceed as with water samples.

F Matrix Spike/Matrix Spike Duplicate (MS/MSD)

An MS/MSD is prepared at a frequency of 5% of all samples analyzed in a given matrix (water or soil). If the MS/MSD recoveries are not 75-125%, and all LCS recoveries are acceptable, flag the data as indicative of possible matrix interference.

G Target analytes are identified as set forth in the method by retention time and characteristic ion comparison. Target analytes will be quantitated using the EICP of the primary characteristic ion using the internal standard technique set forth in the method.

H. Surrogate Recoveries

Calculate the surrogate recoveries for all the samples, blanks, LCS's and matrix spikes. The recoveries should fall within the acceptance limits stated in the method. If the recoveries of both surrogates fall outside the limits established, the analyst should reanalyze the samples in question and/or check the instrument for malfunctions such as leaky purge vessels. Surrogate recovery control charts are also plotted to determine trends in recovery.

XVI. Applicable Documents/References

Test Methods for Evaluating Solid Waste Physical/Chemical Methods, US EPA SW-846, 3rd Edition, Method 8260A.

Volatile Organic Compounds by 8260A

TABLE 1

Internal standards

Pentafluorobenzene
1,4-Difluorobenzene
Chlorobenzene-d5
1,4-Dichlorobenzene-d4

System Monitoring Compounds

Dibromofluoromethane (surr)
Toluene-d8 (surr)
4-Bromofluorobenzene (surr

Target Compounds

Dichlorodifluoromethane
Chloromethane
Vinyl chloride
Bromomethane
Chloroethane
Trichlorofluoromethane
Acrolein
Diethyl ether
Acetone
Acetonitrile
1,1-Dichloroethene
Methyl Iodide
Allyl Chloride
Carbon disulfide
Methylene Chloride
Acrylonitrile
2-Methoxy-2-methylpropane(MTBE)
trans-1,2-Dichloroethene
1,1-Dichloroethane
Vinyl acetate
Propionitrile
Chloroprene
2-Butanone
Methacrylonitrile
cis-1,2-Dichloroethene
2,2-Dichloropropane
Isobutanol
Bromochloromethane
Chloroform
1,1,1-Trichloroethane
1,2-Dichloroethane
1,1-Dichloropropene
Benzene
Carbon Tetrachloride
1,2-Dichloropropane
Trichloroethene
Methylmethacrylate
Dibromomethane
1,4-Dioxane
Bromodichloromethane
Bis(chloromethyl) ether
Ethylmethacrylate
2-Hexanone
2 Chloroethyl vinyl ether
4-Methyl-2-Pentanone
cis-1,3-Dichloropropene
Toluene
1,1,2-Trichloroethane
trans-1,3-Dichloropropene
1,3-Dichloropropane
Dibromochloromethane
1,2-Dibromoethane
Tetrachloroethene
Chlorobenzene
1,1,1,2-Tetrachloroethane
Ethylbenzene
m&p-Xylene
Bromoform
Styrene
o-Xylene
cis-1,4-dichloro-2-butene
Isopropylbenzene
trans 1,4 Dichloro 2 Butene
1,2,3-Trichloropropane
Bromobenzene
1,1,2,2 Tetrachloroethane
n-Propylbenzene
2-Chlorotoluene
1,3,5-Trimethylbenzene
4-Chlorotoluene
tert-Butylbenzene
Pentachloroethane
1,2,4-Trimethylbenzene
sec-Butylbenzene
1,3-Dichlorobenzene
4-Isopropyltoluene
1,4-Dichlorobenzene
Dicyclopentadiene
1,2,3-Trimethylbenzene
n-Butylbenzene
1,2-Dichlorobenzene
Hexachloroethane
1,2-Dibromo-3-chloropropane
1,2,4-Trichlorobenzene
Naphthalene
Hexachlorobutadiene
1,2,3-Trichlorobenzene

Method 8260 - Table 2

			QIon	RT
GASES MIX @ 100PPM (RESTEK 502.2 MIX#1)				
2	T	Dichlorodifluoromethane	85	6.94
3	P	Chloromethane	50	7.49
4	C	Vinyl chloride	62	7.81
5	T	Bromomethane	94	8.72
6	T	Chloroethane	64	8.93
7	T	Trichlorofluoromethane	101	9.73
8260 MIX 1 @ 100PPM (RESTEK 502.2 MIXES 2-6 PLUS KETONES)				
10	T	Acetone	43	10.24
12	C	1,1-Dichloroethene	96	10.78
16	T	Methylene Chloride	84	11.36
19	T	trans-1,2-Dichloroethene	96	12.21
20	PM	1,1-Dichloroethane	63	12.70
24	T	2-Butanone	43	13.32
25	T	cis-1,2-Dichloroethene	96	13.68
27	T	2,2-Dichloropropane	77	13.85
28	T	Bromochloromethane	128	14.11
29	C	Chloroform	83	14.04
32	T	1,1,1-Trichloroethane	97	14.92
33	T	1,2-Dichloroethane	62	15.20
35	T	1,1-Dichloropropene	75	15.23
36	M	Benzene	78	15.52
37	T	Carbon Tetrachloride	117	15.46
38	C	1,2-Dichloropropane	63	16.76
39	M	Trichloroethene	130	16.67
41	T	Dibromomethane	174	16.99
43	T	Bromodichloromethane	83	17.05
46	T	2-Hexanone	43	19.21
49	T	4-Methyl-2-Pentanone	43	17.75
50	T	cis-1,3-Dichloropropene	75	17.95
51	CM	Toluene	92	18.82
52	T	1,1,2-Trichloroethane	83	19.05
53	T	trans-1,3-Dichloropropene	75	18.74
54	T	1,3-Dichloropropane	76	19.42
55	T	Dibromochloromethane	129	19.95
56	T	1,2-Dibromoethane	107	20.35
57	T	Tetrachloroethene	166	20.10

Method 8260 - Table 2 (cont.)

			QIon	RT
8260 MIX 1 @ 100PPM (RESTEK 502.2 MIXES 2-6 PLUS KETONES)(cont.)				
58	PM	Chlorobenzene	112	21.33
59	T	1,1,1,2-Tetrachloroethane	131	21.39
60	C	Ethylbenzene	91	21.54
61	T	m&p-Xylene	106	21.76
62	P	Bromoform	173	22.84
63	T	Styrene	104	22.50
64	T	o-Xylene	106	22.57
66	P	1,1,2,2-Tetrachloroethane	83	23.25
67	T	Isopropylbenzene	105	23.40
69	T	1,2,3-Trichloropropane	75	23.53
70	T	Bromobenzene	156	24.15
73	T	n-Propylbenzene	91	24.35
74	T	2-Chlorotoluene	91	24.63
75	T	1,3,5-Trimethylbenzene	105	24.76
76	T	4-Chlorotoluene	91	24.76
77	T	tert-Butylbenzene	119	25.69
79	T	1,2,4-Trimethylbenzene	105	25.77
80	T	sec-Butylbenzene	105	26.36
81	T	1,3-Dichlorobenzene	146	26.72
82	T	4-Isopropyltoluene	119	26.73
83	T	1,4-Dichlorobenzene	146	26.98
84	T	n-Butylbenzene	91	28.05
85	T	1,2-Dichlorobenzene	146	28.05
87	T	1,2-Dibromo-3-chloropropane	75	30.40
88	T	1,2,4-Trichlorobenzene	180	33.71
89	T	Naphthalene	128	34.19
90	T	Hexachlorobutadiene	225	34.50
91	T	1,2,3-Trichlorobenzene	180	35.01
ACROLEIN & ACRYLONITRILE @ 500PPM				
8	T	Acrolein	56	10.07
17	T	Acrylonitrile	53	11.26
2-CHLOROETHYLVINYL ETHER @ 200PPM				
48	T	2 Chloroethyl vinyl ether	63	17.50

Method 8260 - Table 2 (cont.)

			QIon	RT	
8260MIX 2 @ 100/500/1000PPM					
11	T	Acetonitrile	41	10.68	500PPM
14	T	Allyl Chloride	41	11.29	
22	T	Propionitrile	54	13.06	500PPM
23	T	Chloroprene	53	13.08	
26	T	Methacrylonitrile	67	13.51	500PPM
30	T	Isobutanol	43	14.04	1000PPM
40	T	Methylmethacrylate	41	16.81	
42	T	1,4-Dioxane	88	16.99	1000PPM
45	T	Ethylmethacrylate	69	18.94	
65	T	cis-1,4-dichloro-2-butene	88	22.86	74PPM
68	T	trans 1,4 Dichloro 2 Butene	53	23.53	118PPM
78	T	Pentachloroethane	117	25.62	
86	T	Hexachloroethane	117	29.84	
8260MIX 3 @ 100PPM					
9	T	Diethyl ether	59	10.24	
13	T	Methyl Iodide	142	11.11	
15	T	Carbon disulfide	76	11.60	
18	T	2-Methoxy-2-methylpropane(MTBE)	73	12.12	
21	T	Vinyl acetate	43	12.70	

STANDARD OPERATING PROCEDURE

Nitrate and Nitrate/Nitrite
Automated Alpkem Method

SOP Number	HO-I-014-B
Author	Bruce Brown
Effective Date	January 14, 1997
Supersedes	HO-I-014-A

Approvals:

Bruce Brown 1/23/97

General Chemistry Supervisor Date

1/23/97

Quality Assurance Officer Date

STANDARD OPERATING PROCEDURE

Nitrate and Nitrate/Nitrite
Automated Alpkem Method

SOP Number HO-I-014-B

Effective Date: January 14, 1997

I. SCOPE AND APPLICATION

This method pertains to the determination of nitrite singly, or nitrite and nitrate combined in surface and saline waters, and domestic and industrial wastes. The applicable range of this method is 0.05 to 10.0 mg/L nitrate-nitrite nitrogen. The range may be extended with sample dilution.

II. SUMMARY OF METHODS

The buffered (pH 8.5) sample is passed through a column containing copperized cadmium to reduce nitrate to nitrite. The nitrite (originally in the sample plus reduced nitrate) is determined by diazotization with sulfanilamide and coupling with N-(1 naphthyl)-ethylenediamine dihydrochloride to form an azo dye measured at 540 nm.

III. INTERFERENCES

Pre-filter turbid samples prior to analysis. EDTA is added to eliminate interference from iron, copper or other metals. Adjust samples to pH 5 to 9 with either conc. HCl or NH_4OH. Samples containing large concentrations of oil and grease must be extracted with an organic solvent. Samples containing sulfide cannot be determined by this method without first removing the sulfide by precipitation with cadmium nitrate. Norwitz and Keliher (3,4) have compiled a comprehensive study of interferences in the spectrophotometric analysis of nitrite.

IV. SAMPLE HANDLING AND PRESERVATION

Determine unpreserved samples immediately upon collection. Samples with 24-hours require refrigeration at 4°C. Samples may be preserved with sulfuric acid to a pH of 2.0. Holding time is 28 days. Do not preserve samples with mercuric chloride.

V. SAFETY INFORMATION

Each chemical compound used in this SOP should be treated as a potential health hazard. Care should be used while handling samples because of toxicity. Exposure to these substances must be reduced to the lowest possible level by whatever means available (i.e., gloves, lab coats, eye protection, fume gods). Reference files of OSHA regulations and Material Safety Data Sheets (MSDSs) are available to all personnel involved in this analysis.

VI. RESPONSIBILITIES

A. Analysts

1. All analysts performing this procedure are responsible for strict adherence to the SOP.

2. Analysts are responsible for ensuring that any deviations to this SOP are reported.

3. Analysts are responsible for reporting to the section supervisor any required revisions to the SOP.

B. Department Supervisors/Managers

1. The department supervisor/manager is responsible for ensuring adherence to this SOP.

2. The department supervisor/manager is responsible for performing an annual review of this SOP and reporting any required revisions to the Quality Assurance Officer.

C. Quality Assurance Officer (QAO)

1. The QAO is responsible for conducting semi-annual laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Regional Management and Corporate Quality.

2. The QAO is responsible for ensuring that all revisions to the SOP are implemented.

3. The QAO is responsible for determining distribution of and maintenance of document control for this SOP.

VII. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. Required revisions will be incorporated at the time of review.

C. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

VIII. DISTRIBUTION

Distribution of this SOP will be determined by the Quality Assurance Officer.

IX. APPARATUS

Alpkem autoanalyzer

X. REAGENTS

A. Stock Ammonium Chloride-EDTA buffer, pH 8.5 (1 L)

1. Ammonium Chloride - 85 g

   NH_4Cl (FW 53.50)

2. Disodium Ethylenediamine Tetraacetate - 0.1 g

   $(HO_2CCH_2)_2N(CH_2)_2N(CH_2CO_2Na)_2 \cdot 2H_2O$ (FW 372.25)

3. Ammonium Hydroxide, conc. - to pH 8.5
   NH_4OH (FW 35.05)

B. Working Ammonium Chloride-EDTA

1. Stock Buffer - 200 mL

2. Brij-35®, 30% - (4 drops) 0.2 mL

Add 4 drops Brij-35® to each 200 mL of stock buffer required. Mix well.

C. Color Reagent - 500 mL

1. Phosphoric Acid, conc. - 50 mL
H_3PO_4 (FW 98.00)

2. Sulfanilamide - 20 g
$H_2NC_6H_4SO_2NH_2$ (FW 172.21)

3. N-1-naphthylethylenediamine Dihydrochloride - 1 g
$C_{10}H_7NHCH_2NH_2°2HC1$ (FW 259.18)

4. Deionized Water

Cautiously add 50 mL of concentrated phosphoric acid to 400 mL of deionized water (while stirring) contained in a 50 mL volumetric flask. Dissolve 20 g of sulfanilamide and 1 g N-1-naphthylethylene-diaminedinydrochloride in the phosphoric acid solution. Dilute to the mark with deionized water. Store in brown bottle and keep in the dark when not in use. Reagent is stable for several months.

D. Stock 100 mg/L Nitrate Nitrogen Standard (1 L)

1. Potassium Nitrate - 0.7218 g
KNO_3 (FW 101.11)

2. Deionized Water

3. Chloroform - 2 mL
$CHC1_3$ (FW 119.38)

Dissolve 0.7218 g of potassium nitrate in approximately 900 mL of deionized water contained in a 1 L volumetric flask. Dilute the solution to the mark with deionized water. Preserve the stock standard with 2 mL of chloroform. Store at 206°C.

E. Stock 100 mg/L Nitrate ICV Standard

1. Sodium Nitrate - 0.6068 g

   $NaNO_3$

2. Deionized Water

3. Chloroform - 2 mL

   Dissolve 0.6068 g of sodium nitrate in approximately 900 mL of deionized water contained in a 1 L volumetric flask. Dilute the solution to the mark with DI water. Preserve the stock standard with 2 mL of chloroform. Store at 2-6°C.

F. Stock 100 mg/L Nitrite Nitrogen Standard

1. Potassium Nitrite - 0.6072 g

   KNO_2 (FW 85.11)

2. Deionized Water

3. $CHCl_3$

   Dissolve 0.6072 g of dry potassium nitrite in approximately 900 mL of deionized water contained in a 1 L volumetric flask. Dilute the solution to the mark with deionized water. Preserve the stock standard with 2 mL of chloroform and refrigerate at 2-6°C.

G. Stock 100 mg/L Nitrite ICV Standard

1. Sodium Nitrite - 0.4923 g

   $NaNO_2$

2. Deionized Water

3. Chloroform - 2 mL

   Dissolve 0.4923 of dry sodium nitrite in approximately 900 mL of deionized water contained in a 1 L volumetric flask. Dilute the solution to the mark with deionized water. Preserve the stock standard with 2 mL of chloroform and refrigerate at 2-6°C.

H. Granulated Cadmium 30-60 mesh

1. 2% Copper Sulfate - 1 L

2. Copper Sulfate - 20 g
   $CuSO_4°5H_2O$ (FW 249.69)

3. Deionized Water

   Dissolve 20 g of copper sulfate in 500 mL of deionized water contained in a 1 L volumetric flask. Dilute to the mark with deionized water.

I. 6N Hydrochloric Acid

1. Hydrochloric Acid, conc. - 50 mL
   HCI (FW 36.46)

2. Deionized Water

   Dilute 50 mL of hydrochloric acid contained in a 100 mL volumetric flask to the mark with deionized water.

J. Preparation of Copperized Cadmium

1. Clean cadmium granules with 6N HCI. Cadmium should appear silver. Rinse well with deionized water.

2. Swirl cleaned cadmium in 50 mL portions of 2% copper sulfate for 5 minutes or until blue color partially fades. Decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.

3. Gently wash the copperized cadmium with deionized water to remove all the precipitated copper. Cadmium should appear black.

K. Preparation of Cadmium Reductor Column

Reduction column is a glass tube 0.050"ID, 0.140"OD, 2 1/2" long.

Exhibit A

1. Remove tubing assembly from glass column.

2. Insert a plug of pyrex glass wool into one end of the glass column.

3. Replace the tubing assembly on the same end as the glass wool. The glass wool prevents cadmium granules from migrating.

L. Column Packing

1. Hold the glass column vertically. The polyethylene extension should be parallel to the glass column.

Exhibit B

2. Using a wash bottle or a pipet, fill the column/tubing assembly with deionized water.

3. Using a glass Pasteur pipet (5-3/4" - available from Kimble, a division of Owens, Illinois - Toledo, Ohio 43666). Carefully aspirate a slurry of copperized cadmium into the pipet.

4. Insert the pipet tip into the top of the glass column.

5. Allow the cadmium to fall into the column. Tap the column gently to facilitate even packing. Avoid trapping air bubbles in column.

6. Repeat steps 3 through 5 until column is filled 1/8 - 1/4" from top.

7. Pack a duplicate column and connect in series with first column.

M. Installation of Column on Manifold

After stable hydraulics are obtained on water:

1. Pump working buffer. Allow to stabilize 5-10 minutes.

2. Verify debubble fitting is removing all bubbles prior to column position.

3. Turn the 302 pump **OFF**. Using an awl, gently remove the jumper tubing from the manifold.

4. Install the 2 packed columns in series and verify that no gaps exist between the debubbler and the columns.

5. Turn the 302 pump **ON**. Allow hydraulics to stabilize.

N. Column Removal and Storage

1. With buffer still being pumped through the column, turn the pump **OFF**.

2. Remove the column and replace the jumper. Turn on the pump and flush the manifold with deionized water.

3. Construct a second tubing assembly identical to the column outlet and place on the column inlet.

4. Using a syringe, gently back-fill the column with buffer so inlet tubing is filled.

5. Connect inlet and outlet tubing with a N-13 nipple. Verify there are no bubbles trapped in the assembly.

O. Operating Notes

1. The column may be conditioned by running a mid scale standard through the manifold for 10 - 15 minutes.

2. Column life expectancy data is unavailable at this time. It is recommended that a nitrite standard of the same nominal concentration as the high scale standard be used as a check or column reduction efficiency.

3. Two columns can be put in series to boost sample exposure and column efficiency.

P. Nitrate Calibration Standard

All standards are brought to volume in a 100 mL volumetric flask with DI water.

Calibration blank:		100 mL DI water
Standard 1:	(0.1 mg/L)	0.1 mL of 100 ppm NO_3 standard
Standard 2:	(0.5 mg/L)	0.5 mL of 100 ppm NO_3 standard
Standard 3:	(1.0 mg/L)	1.0 mL of 100 ppm NO_3 standard
Standard 4:	(2.0 mg/L)	2.0 mL of 100 ppm NO_3 standard
Standard 5:	(5.0 mg/L)	5.0 mL of 100 ppm NO_3 standard
Standard 6:	(10.0 mg/L)	10.0 mL of 100 ppm NO_3 standard
ICV:	(5.0 mg/L)	5.0 mL of 100 ppm NO_2 ICV standard
NO_2:	(5.0 mg/L)	5.0 mL of 100 ppm NO_2 standard Column Efficiency Check
Low D-L STD	(0.05 mg/L)	0.05 mL of 100 ppm NO_3 standard - when needed

Q. Nitrite Calibration Standard

All standards are brought to volume in a 100 mL volumetric flask with DI water.

Calibration blank:		100 mL DI water
Standard 1:	(0.1 mg/L)	0.1 mL of 100 ppm NO_2 standard
Standard 2:	(0.5 mg/L)	0.5 mL of 100 ppm NO_2 standard
Standard 3:	(1.0 mg/L)	1.0 mL of 100 ppm NO_2 standard
Standard 4:	(2.0 mg/L)	2.0 mL of 100 ppm NO_2 standard
Standard 5:	(5.0 mg/L)	5.0 mL of 100 ppm NO_2 standard
Standard 6:	(10.0 mg/L)	10.0 mL of 100 ppm NO_2 standard
ICV:	(5.0 mg/L)	5.0 mL of 100 ppm NO_2 ICV standard

XI. PREP PROCEDURE

A. Prep

1. Adjust 50 mL of sample to pH 5 to 9 with either conc. HCI or NH_4OH.

2. Place a small portion of the pH adjusted sample into a disposable beaker and test for Nitrate and Nitrite with an EM Quant Nitrate test strip. This is to estimate the amount of analyte in the sample so that appropriate dilutions can be made on the initial run. This will minimize reruns and help preserve the column life. The test strip ranges are given as NO_3 to convert this value to N:

$$\frac{\textit{Test Strip value (mg/L as } NO_3\textit{) x 14}}{62} = \textit{Value as N}$$

3. Use the calculated value to estimate dilutions that will put the peak height in the upper 2/3 of the 0.1 to 10.0 mg/L scale.

XII. ALPKEM COLOR DEVELOPMENT

A. Set the spectrophotmeter and the sampler to the following parameters from the Alpkem manual and proceed through the Alpkem procedure that follows.

B. Clean the platens and the pump rollers with isopropyl alcohol.

1. Check the platens for excessive wear and replace them if necessary.

2. The pump roller carriage may be turned by hand for access to all of the rollers to clean them after clearing the previous test tubing.

C. Install the appropriate board and reagent lines..

1. Retrieve the board from the drawer and carefully unwrap the reagent lines.

2. Set the board into the module, bringing the reagent lines to drape in front of the module.

3. Inspect the reagent lines and connections for wear, splits, cracks, and solid clogs, and replace if necessary.

4. Inspect the hoses for wear at the point of the pump roller crossing and replace them if misshapen and flattened.

5. Inspect the mixing coils, manifolds and connectors for cracks, leaks or clogs, and replace or clean them as necessary.

6. Inspect and install, as needed according to the Alpkem diagrams, all the air lines, sampler was feed lines, waste lines and debubbler waste lines.

7. Connect the sample line to the sample probe.

8. Position the reagent, sample, waste, sample wash, debubbler waste and air lines in an arrangement across the pump rollers so that

   a) both sides of each platen will have at least on line under it (use dummy lines if needed)

   b) the lines closest in size share a platen

   c) the lines have no sharp bends or kinks

d) the lines all neatly go to their destinations with a minimum of confusion and tension.

9. Install the platens (if the unit is on, leave one unclamped to keep the pump from starting) using the least worn for the reagent and the sample lines, and the more worn for air, waste and sample wash lines.

10. Place the reagent lines into DI water and/or the appropriate start-up solution bottles.

(See Exhibit)

D. Install the appropriate filters and the flow cell to the spec.

1. Select the appropriate filters from the jar according to the Alpkem diagram.

2. Wipe the filters with KimWipes and gently remove any particles of dust with air.

3. Screw the filters into the special housing (glass side in) until they are snug.

4. Select the appropriate flow cell according to the Alpkem diagram and inspect it for cleanliness (gently back flush if necessary using syringe). Make sure the flow cell is completely dry after flushing it by wiping with a KimWipe.

5. Install the flow cell drain tube to the side of the flow cell closest to the spec and connect the other side of the flow cell to the flow cell feed line from the last mixing coil.

6. Gently install the flow cell to the sample side of the spec positioned between the filter and the light source. Tighten this snugly with an allen wrench. Install the reference cell to the reference filter and the light source; tighten this snugly with an allen wrench.

7. Place the flow cell drain tube and any other waste lines in the waste hole on the board.

E. Run the system on the appropriate start up solutions.

1. Verify that the front module switches are on for the sampler, light source, and the pump module.

2. Clamp all of the platens down and turn on the system with the switch located on the master power supply box. The pump should immediately start. If not,

   a. Check that the platens are securely clamped

   b. All the appropriate switches are on

   c. All the plugs into the master power supply box are securely tied in.

   d. Turn off the system and check the fuse located in the main power plug to the master power supply box.

3. Verify that the light source is illuminated, if not:

   a. Check the light source "on" switch

   b. Check the light source plug to the power box

   c. Check the light source bulb by unscrewing the light source cable from the back of the module and replace it if blown.

4. Verify that the spectrophotometer is functioning by seeing a voltage display. If not,

   a. Check all on/off switches

   b. Check all of the plugs

   c. Verify the light source

   d. Check the master fuse.

5. Make the initial calibration settings

   a. Put the bubble gate switch on the side of the spectrophotometer in the "on" position if not using a debubbler on the flow cell, and "off" if one is used.

   b. Set the damping control on top of the spec to position indicated by Alpkem spectrophotometer parameters.

   c. Set the calibration control on the top of spec to 60.

   d. Allow the system to run until all the air is out of all lines and coils with evenly spaced bubbles going through the flow cell. Also, allow the heat bath to come to the correct temperature at this time.

F. Adjust the bubble phasing to achieve and acceptable pattern (if a debubbler is not used on the flow cell)

1. The bubble phasing control is a selector switch located in the back of the pump modules (reference manual). Turning the switch allows preset adjustment of the phasing between the pumps downstroke and the valves injection of the bubble into the manifold. The optimum theoretical setting is a bubble injection simultaneous with the pumps downstroke, but often something slightly different is what is required. Strokes are denoted with a click sound. Adjust the control so that the bubbles injected are:

   a. Single - split bubbles are out of phase with stroke

   b. Correct size and equal in size

   c. Oval (not round) and regularly spaced

   d. There are no intermediate bubbles (between clicks)

   e. There are no bubble splits or additions as the bubbles flow past reagent injection manifolds.

   Note: Air may also come through reagent lines if the line is not down in the solution, or there are leaks or cracks in the he connections.

2. If the bubble pattern is unacceptable after setting phasing with strike:

   a. Check the surfactant levels in the appropriate reagents and start up solutions. Too little surfactant increases friction and drag on bubbles that may split them. This also increases back pressure problems that keep the bubbles out of phase and possibly irregularly spaced.

   b. Check for back pressure problems from

      (1) Clogs in the lines from particles and kinks in tubing

      (2) Clogs in flow cell or waste lines

      (3) Incorrect size of poly tubing used in lines

      To isolate where a clog or kink is, while system is running disconnect one section at a time starting from flow cell drain and working back. When pressure is relieved, there will be a notable surge in flow. Clean or replace the part of the sample line involved.

   c. Adjust the length of tubing

      (1) On the air line to the manifold, try different length and diameter poly tubing to help balance pump strength against line pressure. Sometimes a yellow-orange pump tube works well in this spot.

   d. If bubbles are being split at the reagent injection points, verify that manifold is not defective by replacing it with a new one.

G. Calibrate the chart recorder and monitor the baseline on start up solutions.

   1. Turn the chart recorder switch "on"

   2. Remove the cap from the pen (connected to channel)

   3. Lower the pen to the paper

   4. Verify that the chart speed is set at 1 cm/min and going in down direction

5. On the computer, press [ENTER} till the Primary Commands are displayed. Select E: Utility Programs

6. Under Utility Programs, select 3: Scale

   a. Enter sampler designator: A

   b. Enter "5" volts and verify pen has gone full scale to 5 volts on chart. If low or high, adjust with calibration (var/cal) knob on appropriate pen.

   c. Enter "0" and verify pen has gone to "0". If not, adjust with ←o→ knob on recorders.

   d. Recheck "5" and "0" volts to verify they are both in, then check other voltages. (EX. 2.5, 0.25, etc.)

   e. Press [ENTER] again without a voltage and the program will go to "sample" and the chart recorder will directly monitor the voltage off of the spectrophotometer.

   f. If baseline is not smooth, check

      (1) Quality of start up solutions
      (2) If all unnecessary air is out of the system
      (3) Light source is on
      (4) Fiber optic end in flow cell holder is clean and flow cell holder is secure for sample and reference
      (5) Flow cell is clean
      (6) Bubble pattern is good and consistent
      (7) Bubble gate delay switch is in correct position
      (8) Bubble gate delay is adjusted*

      Note: Bubble gate delay determines what time, after a bubble passes through the flow cell, the spec will make a reading. The best theoretical time is 6/10 of a second. Adjust gate delay screw verifying that indicator light on top of spec flushes between passing bubbles. Then use baseline to fine-adjust, making as smooth as possible. Noise must be eliminated sufficiently to discern a detection limit of 0.05 mg/L.

H. Run reagents and monitor baseline

Add the reagents one at a time to the system and if there is a noticeable increase in noise, filter or remake the reagent.

Note: A rise in voltage of baseline is normal.

I. Initial spectrophotometer setup

1. After all reagents are in the system and an acceptable baseline is achieved, put the spectrophotometer function switch in the "sample" position. The voltage displayed is for the sample flow cell only. Use the sample gain controls to adjust the voltage to read 5.00 volts.

2. Put the function switch into the "absorbance" position. The voltage displayed is the comparative difference between the sample cell and the reference cell (the reference cell must be tightened so as not to vibrate). Adjust the reference gain controls to bring the voltage to 0.25 volts. Monitor the baseline as in step F to verify the chart recorder is also reading 0.25 volts, and that there is no drift across time. If there is a baseline drift, check the stability of the sample and reference flow cell to see that there are no leaks around the flow cells. Other causes for drift could be reagent quality and the sampler was reservoir cleanliness. Once a stable baseline is achieved and the voltage is adjusted to 0.25, make a dwell determination.

J. Determine Dwell Time

1. Place a sample cup containing high range standard 6 in the sampler tray and place the tray on the sampler in the position for the cup to be sampled.

2. From the Primary Commands menu, select E: Utility Program commands

3. When you press the [ENTER} key, the following prompt will appear:

Enter Sample Designator (A/B) >

4. Enter "A" or "B" to indicate which sample (and Analytical Configuration File) you want to determine dwell times for, or simply press [ENTER] to abort the sequence. In either case, the program will return to the Menu E display. Meanwhile, if you entered a valid sampler designator, the sampler probe will sample from the dwell cup for the sample time in effect for the sampler, and signals from all active data channels for the sampler will be displayed to the system strip chart recorders.

5. When the peak from the dwell sample appears in the signal on each data channel, the system will wait for the failing edge of the peak and then send the strip chart pen for that channel to zero. At the same time, the message

   Channel N: Dwell Found, Dwell Time = XXX Seconds

   will be displayed in the real time message window on the CRT. When you see this message, you may have the dwell time value displayed by again entering "1" at the Menu E display to activate the Determine Dwell Time utility. The program will now display the following message and prompt.

6. **There are Dwell Times in the Queue**
   Print Hard Copy (Y/N)?

   Enter "Y" if you want to have the dwell times printed on the printer. Otherwise, enter "N" or just press the [ENTER] key. All dwell times in the queue will then be displayed on the CRT in the format shown below. If you selected hard copy, the same information will be printed on the printer. All values displayed are in seconds.

Channel Number	Dwell Time
N	XXX
M	YYY

Press Return to Continue

K. Readjust the spectrophotometer calibration

Once the high standard peak height is observed on the chart recorder from the dwell determination, adjust the calibration control to allow the high standard peak height to measure 90 to 95% across the 5 volt scale. After the calibration has been adjusted, readjust the spectrophotometer to a baseline of 0.25 volts as in Step L.

L. Modify the Analytical Configuration File (ACF)

1. To modify the ACF with "4" in response to the Menu "B" display. The program will prompt for a file name as follows:

Enter Filename >
Enter <Nitrate> as the filename

Do you wish to add/delete channels (Y/N) >
Press [ENTER} to decline, then press [ENTER] until the frame with the dwell time is displayed. At this frame, enter "M" for modify. A series of prompts will display which is declined by [ENTER]. Proceed through the prompts until the dwell time prompt at which "Y" is entered. The prompt will then request the new dwell time to be entered at which the recent dwell determination in seconds will be entered.

Enter "E" to exit the sequence and respond to the following prompt.

Save modified file (Y/N) >
Enter "Y"

Enter New Filename >
Press [ENTER] to maintain the old filename

Do you want to activate this file (Y/N)? >
Enter "Y" to activate the file

M. Make an initial run using the cadmium column, the Nitrate analytical configuration file, the Nitrate calibration standards, with the Nitrite column efficiency standard, and all of the samples. The results from the run will be considered the initial Nitrate/Nitrite results provided the Nitrite column efficiency is ± 5.0% of the theoretical value.

N. Make a second run without the cadmium column using the Nitrite calibration standards and the Nitrite-H analytical configuration file with all the samples. The results from this run will be considered the Nitrite verification results and are used to determine the Nitrate and Nitrate/Nitrite results in the calculations.

O. In preparing each run, observe the following QA requirements:

1. Initial Nitrate/Nitrite Run	QA Control Limits
a. Calibration Blank	<0.1 mg/L
b. 6 Nitrate calibration standards	correlation coefficient ≥ 0.998
c. 5.0 mg/L Nitrate ICV standard	± 10% of Theoretical Value
d. 5.0 mg/L Nitrite column efficiency standard	If > 5.0% from the theoretical value, the column efficiency must be factored into the calculation.
e. Duplicate sample every 10 samples	RPD ≤ 20%
f. Matrix Spike every 10 samples	MSR ± 25%
g. A mid-range continuing calibration verification (CCV) standard every 10 samples	± 10% of theoretical value
h. A continuing calibration blank (CCB) every 10 samples	< 0.1 mg/L

2. Nitrite verification run	QA Control Limits
a. Calibration blank	<0.1 mg/L
b. 6 Nitrite calibration standards	correlation coefficient ≥ 0.998
c. 5.0 mg/L Nitrite ICV standard	± 10% of theoretical value
d. A duplicate sample every 10 samples	RPD = ≤ 20%
e. A midrange continuing calibration verification (CCV) every 10 samples	± 10% of theoretical value
f. A continuing calibration blank (CCB) every 20 samples	< 0.1 mg/L

P. Create sample identification file

1. Turn on the computer disk drive, screen and printer
2. After warm up and 640 KB display (C:\>), type "Alpkem" [ENTER]
3. Strike [ENTER] key when ready
4. Enter appropriate ACF file ([ENTER] to bypass 2nd channel)
5. Under primary commands, select **A: Create File**
6. Under **A: Create File,** select **1: Sample Identification File**
7. Enter filename: Month, Day, Year and Number of days run (ex. 02119101 -- February 11, 1991, 1st run of day)
8. Enter comment: Name of parameter to be run and any applicable explanations
9. Apply constant dilution factors? Yes
10. Prompt for dilute factors? No [ENTER]
11. Apply constant sample weights? [ENTER]
12. Prompt for sample weights? [ENTER]
13. Enter constant dilution factor: Usually 1.0
14. Do you wish sequential sample ID number? [ENTER]
15. Enter sample ID for Cup #2: Standard 6 (Highest range standard)
16. Enter rest of run using 2 of each calibration standards listed in ACF (separate each set by blanks). Then enter the samples with their QA, and CCVs and CCBs.

Q. Prepare the sample tray according to the Sample Identification File.

1. Fill each 2 mL cup completely.

2. Filter all sample cups with a 0.45 micron in-line polyethylene filter connected to a 10 cc syringe.

3. Place the completed tray on the sampler with cup #1 in position to be sampled when the run begins. Press the "reset" button on the sampler to ensure the tray is in the correct position.

R. Inspect the reagents and the chart paper on the chart recorder to ensure there are sufficient quantities of both to supply the entire run.

S. Start the sample run.

1. Return to the Primary command and enter "C". Run samples in response to the **Waiting For command >** prompt.

2. Select "1: Run" from the C menu and respond to the following prompts:

Enter sample Designator (A/B) >
Enter "A"

Enter Sample ID Filename >
Enter the 8-digit sample identification file name created in section D.7

Do you Wish to Collect Raw Data (Y/N)? >
Enter "Y" to the prompt. A raw data file will be created and preserved for the run.

Enter Operator Initials >
Enter the analysts ID or name

Ready to Run (Y/N)? >
When "Y" is entered at the prompt, the sampling begins, so be sure the system is completely ready to start. The peak heights will be monitored and displayed on the computer screen automatically unless [ENTER] is pressed at the **Press Return to Stop Monitoring >** prompt.

T. Rerunning Samples

If peak heights are over range or distorted due to matrix or a sampling problem, reruns may be added to the end of the run as long as the sampler has not reached the last cup on the run by responding to the following prompts:

Enter "3" in response to the Menu C display.

Enter Sampler Designator >
Enter "A"

Enter Cup Number >
Enter the number of the cup to be redetermined. The program will repeat this prompt until pressing [ENTER] or until 40 cup numbers have been entered. The same cup number may be entered more than once to redetermine the same sample at different dilutions.

Cup Y Redetermination of X Enter Dilution Factor for "NNNNN" >
The program repeats this prompt for each cup that is added to the run. In this line, "X" represents the original cup number and "y" is the new cup number being added to the run. NNNNN is the sample identifier for "X" being assigned to "Y" prefixed with an ampersand (&) to indicate on the report that it is a redetermination. Enter any number up to 10 characters in length to indicate any dilutions or simply press [ENTER] if no dilution is being made. When al prompts for dilutions have been responded, the program will automatically update the Sample Identification File and the sampler stop count and return to menu display.

Note: This entire entry sequence must be completed and the program returned to menu C before the system will recognize the request to run additional samples.

2. Prepare the additional sample cups using the dilutions indicated above and placing them in the correct positions on the sampler tray.

U. Obtaining Results

1. Select Menu **D: Print Hard Copy** Commands from the Primary Commands, then select **1: Plateau Data** File and respond to the following prompts:

Enter Filename >
Enter the 8-digit number used to create the Sample ID file for the run. Then select **1: Final Results** from the menu displayed.

Suppress Flags on Report (Y/N)? >
Enter "Y" unless the flags explained in Appendix C of the Alpkem manual are useful in evaluating the data.

Redirect Printer Output (Y/N)? >
Enter "N" to this prompt unless it is helpful to preview the report on the computer screen before the report is printed. The printer will begin printing the results immediately after "N" or will display the Plateau Data Reports menu again.

V. Before turning system off, run DI water through the system and all reagent lines for 15 minutes. After turning the systems off, remove all platens and release pump tube pressure from the pump rollers.

XIII. CALCULATIONS

A. A = initial nitrate/nitrite results (times any dilution factor) from the run with the cadmium column using Nitrate Calibration Standards.

B. B = The Nitrite verification results (times any dilution factor) from the second run without the cadmium column using Nitrite calibration standard.

C. If the Nitrite column efficiency standard is equal to or less than ± 5.0%

1. Nitrate mg/L as N = A - B
2. Nitrate/Nitrite mg/L as N = A

D. If the Nitrite column efficiency standard is greater than ± 5.0%
   1. Nitrate mg/L as N = A - B (column efficiency)
   2. Nitrate/Nitrite mg/L as N = Nitrate result + B

XIV. REFERENCES

A. Alpkem Method Number A303-5171-07

B. Standard Methods for the Examination of Water and Wastewater, 14th Edition, 1975. APHA-AWWA-WPCP, p. 365.

C. Methods for Chemical Analysis of Water and Wastes, March 1984, EPA-600/4-79-020, "Nitrogen, Ammonia" Method 351.2 (Colorimetric, Automated Phenate) STORET NO. Total 00610, Dissolved 00608.

D. Norwitz, G., Keliher, P.N., Study of Interferences in the Spectrophotometric Determination of Nitrite Using Composite Diazotisation - Coupling Reagents, Analyst, June 1985, Vol. 110, p. 689-694

E. Norwitz, G., Keliher, P.N., Study of Interferences in the Spectrophotometric Determination of Nitrite Using Composite Diazotisation - Coupling Reagents, Analyst, September 1986, Vol. 111, p. 1033-1037.

F. Methods for Chemical Analysis of Water and Wastes, March 1984, EPA-600/4-79-020, "Sample Preservation", p. xvii, Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45286

STANDARD OPERATING PROCEDURE

METALS BY ICP

SW846 METHOD 6010A

SOP NUMBER	HO-I-033-C
AUTHOR	DAVID ROSE
EFFECTIVE DATE	OCTOBER 5, 1995
SUPERSEDES	HO-I-033-B

APPROVAL

David Rose 10/11/95
Metals Supervisor Date

Russell Morgan 10/11/95
Inorganic Laboratory Manager Date

10-11-95
Quality Assurance Officer Date

10-12-95
Laboratory General Manager Date

I. PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to establish a procedure for the determination of metals by inductively coupled plasma atomic emission spectroscopy under SW-846 method 6010A.

II. SCOPE AND APPLICATION

A. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is utilized for the determination of metals in solution. The method is applicable to a large number of matrices. All matrices, including ground water, aqueous samples, leachates, industrial wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

B. Elements for which this method is applicable are listed in Table I.

III. RESPONSIBILITIES

A. QUALITY ASSURANCE OFFICER

Responsible for reviewing SOPs for method compliance, distributing controlled copies, and maintaining records of distribution.

B. INORGANIC LABORATORY MANAGER

1. Responsible for ensuring that analysts perform analysis according to this SOP.

2. Responsible for reviewing and revising SOPs annually, at a minimum.

C. ANALYST

Responsible for performing the analysis in accordance with the method described in this SOP.

IV. REVIEWS/REVISIONS

This SOP will be reviewed on an annual basis at a minimum.

V. DISTRIBUTION

Distribution of this SOP will be determined by the Quality Assurance Officer.

VI. SUMMARY OF METHOD

A. Prior to analysis, samples must be solubilized or digested using appropriate sample preparation methods (see PACE SOP #s HO-I-031, HO-I-032.).

B. This method describes the sequential or simultaneous multielemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes.

C. Background correction may be required. Background is measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used should be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section VIII should also be recognized and appropriate corrections made as necessary.

VII. SAFETY

A. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file

of material handling data sheet should be made available to all personnel involved in the chemical analysis.

B. Concentrated acids are corrosive and should be used in a laboratory hood when possible. Protective clothing and safety glasses should be worn.

VIII. INTERFERENCES

A. SPECTRAL INTERFERENCES

Spectral Interferences are caused by:

1. Overlap of a spectral line from another element;

2. Unresolved overlap of molecular band spectra;

3. Background contribution from continuous or recombination phenomena;

4. Stray light from the line emission of high-concentration elements.

Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line. Interelement correction factors are used on the simultaneous ICP.

B. PHYSICAL INTERFERENCES

Effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high levels of dissolved solids or high acid concentrations. If physical interferences are present, they may be reduced by diluting the sample. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which effects aerosol flow rate and causes instrument drift. The problem can be controlled by wetting the argon prior to nebulization, or diluting the sample.

IX. APPARATUS AND MATERIALS

A. Themo Jarrel Ash 61E Inductivly Coupled Plasma

B. Perkin Elmer Plasma 40 Emission spectrometer.

C. Liquid argon gas supply.

D. Volumetric flasks - assorted Class A.

E. Pipettes - assorted Class A.

F. Automatic pipettes with disposable tips.

X. REAGENTS

A. Hydrochloric acid concentrated.

B. Hydrochloric acid (1:1). Add 500mL conc. HCL to 400mL DI water and dilute to 1L.

C. Nitric acid concentrated(HNO3), instra-analyzed or equivalent

D. Nitric acid(1:1) Add 500mL conc. HNO3 to 400mL DI water and dilute to 1L.

E. ASTM Type II Water (ASTM D1193)

F. Standard Stock Solutions, purchased (NIST Traceability must be available) or prepared from ultra-high purity grade chemicals or metals (99.99 to 99.999% pure).

G. Calibration Standard Solutions

1. Calibration Standard Preparation

Calibration standards are purchased from vendors and diluted to appropriate volumes. The standards are made in 1% HNO3 and 5% HCL. Standards are diluted to volume for use daily. Verify calibration standards using a second source standard. Some typical calibration standard combinations are listed in Table 3.

2. Calibration Verification Standard

A verification standard is a midpoint calibration standard from another standard source.

XI. SAMPLE PRESERVATION AND HOLDING TIMES

A. SAMPLE PRESERVATION

1. *Water Sample Preservation*

a. Container: polyethylene or glass.

b. Preservation: Sample preservation is performed by the sampler immediately upon sample collection. Use HN03 to bring the pH to <2. Samples to be analyzed for dissolved metals analysis are to be filtered at the time of collection, prior to acidification.

2. Soil and Sediment Preparation

Soils/sediments will be maintained at 4C (± 2) until analysis.

B. HOLDING TIMES FOR WATER AND SOIL/SEDIMENT SAMPLES

The maximum sample holding time for metals is 180 days from sample receipt.

XII. INSTRUMENTAL ANALYSIS

A. Consult instrument manufacturer's user's manuals for specific operational instructions.

B. See Table 2 for an example run sequence.

C. INSTRUMENT CALIBRATION

1. Instrument calibration is to be performed in accordance with the manufacturer's specifications.

2. Instruments must be calibrated once every 24 hours and each time the instrument is set up. The instrument standardization date and time must be included in the raw data.

XIII. QA/QC REQUIREMENTS

A. The QA/QC requirements for the analysis are listed below:

1. Instrument Calibration
2. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)
3. Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)
4. Linear Range Standard (LRS)
5. Interference Check Solutions (ICSA, ICSAB)
6. Method Blank / Preparation Blank (PB)
7. Laboratory Control Sample (LCS)
8. Matrix Spike Sample (S)
9. Duplicate (D)
10. Serial Dilution(L)
11. Internal Standard (sequential only)
12. Interelement Corrections for ICP (simultaneous only)

B. INITIAL CALIBRATION VERIFICATION (ICV) AND CONTINUING CALIBRATION VERIFICATION (CCV)

1. Initial Calibration Verification (ICV)

a. The Initial Calibration Verification Solution(s) should be obtained from a different source than the calibration standards.

b. Immediately after the ICP system has been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of an Initial Calibration Verification Solution(s) at each wavelength used for analysis. When measurements exceed the acceptance limits of 90 to 110% of the true value, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

2. Continuing Calibration Verification (CCV)

a. To ensure calibration accuracy during each analysis run, a continuing calibration verification must be analyzed for every wavelength used for the analysis of each analyte, at a frequency of 10% during an analytical run. The standard must also be analyzed after the last analytical sample. The analyte concentrations in the continuing calibration standard should be at or near the mid-range levels of the calibration curve. The ICV solution can be utilized as the CCV.

b. If the result of the continuing calibration verification is outside the acceptance limits of 90 to 110% of the true value, the instrument should be recalibrated and the preceding analytical samples since the last acceptable calibration verification should be reanalyzed.

C. INITIAL CALIBRATION BLANK (ICB) AND CONTINUING CALIBRATION BLANK (CCB)

A calibration blank is prepared in 1% HNO3 and 5% HCL. The blank must be analyzed at each wavelength used for analysis immediately after every initial and continuing calibration verification. The blank result must be less than the reporting limit for each element analyzed; otherwise, terminate analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples.

D. LINEAR RANGE STANDARD

A high level standard used to determine the upper limit of the ICP calibration. This must be analyzed just prior to initiating sample analysis. The acceptance criteria is 95 to 105% recovery.

E. INTERFERENCE CHECK SOLUTIONS (ICSA AND ICSAB)

ICP Interference Check Samples must be analyzed at the beginning and end of each analysis run or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. The Interference Check Samples consist of two solutions: Solutions A and AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents (see Table 4).

An ICS analysis consists of analyzing both solutions consecutively (starting with Solution A) for all wavelengths used for each analyte reported by ICP. The results of the analytes in Solution AB must fall within 80 to 120% recovery. If not, terminate the analysis, correct the problem, recalibrate the instrument, and reanalyze the analytical samples analyzed since the last acceptable ICS.

F. PREPARATION BLANK

At least one preparation blank (or reagent blank) consisting of deionized water must be prepared and analyzed with each group of samples digested. The element of interest cannot be present at or above the reporting limit in the prep blank. If greater than the reporting limit, redigest and reanalyze all samples associated with the prep blank.

G. LABORATORY CONTROL SAMPLE (LCS)

1. Laboratory Control Samples (LCS) must be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the samples received. One solid or aqueous LCS must be prepared and analyzed for every batch of samples digested (or a minimum of 1 LCS per 20 samples digested).

2. If the % recovery falls outside the laboratory-derived control limits for aqueous LCSs, or the manufacturer's acceptance limits for the purchased soil LCS, the analysis should be terminated, the

problem corrected, and the samples associated with that LCS redigested and reanalyzed.

H. MATRIX SPIKE SAMPLE (S)

1. The matrix spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents). At least one spiked sample must be analyzed for each batch of samples of a similar matrix spike type (i.e., water, soil) at a minimum frequency of 5%. Field blanks cannot be used as spikes. Spike calculations are performed on the original sample if the same sample is designated as the duplicate. The percent recovery of the spike is calculated from the following equation:

$$\% \text{ Recovery} = \frac{(SSR-SR)}{ST} \times 100$$

Where SSR = Spike sample result
SR = Sample result
ST = Spike target

2. When sample concentration is less than the PQL, let SR = 0 only for calculating percent recovery.

3. If the percent recovery is outside 80 to 120% and the LCS was acceptable, flag results as matrix interference.

I. DUPLICATE (D)

1. One duplicate sample must be analyzed from each batch of samples of a similar matrix type (i.e., water, soil).

2. This analysis will be performed at a minimum frequency of 5%. The relative percent differences can be calculated as follows:

$$RPD = \frac{(2)(S-D)(100)}{(S+D)}$$

Where: RPD = Relative Percent Difference

S = Original Sample Value
D = Duplicate Sample Value

3. Acceptable RPD values are defined as follows: < 67% for samples having concentrations < 10X MDL and < 20% for sample concentration > 10X MDL.

J. SERIAL DILUTION

For every digestion group a serial dilution is needed. This is a four fold dilution which must be within 10% of the original determination.

K. INTERNAL STANDARD (SEQUENTIAL ONLY)

An internal standard (usually yttrium) is run with each analysis. The internal standard is used to verify the absence of physical interferences (high dissolved solids, viscosity, surface tension, etc).

L. INTERELEMENT CORRECTIONS FOR SIMULTANEOUS ICP

1. Interelement correction factors must be determined annually. Correction factors for spectral interference due to Al, Ca, Fe, and Mg must be determined for all ICP instruments at all wavelengths used for each analyte reported by ICP. Correction factors for spectral interference due to analytes other than Al, Ca, Fe, and Mg must be reported if they were applied.

2. If the instrument was adjusted in anyway that may affect the ICP interelement correction factors, the factors must be redetermined.

3. Interelemental correction tables are prepared by running 500, 500, 200, 500 ppm, high purity solutions of Al, Ca, Fe, and Mg, and reading their effect on all the other elements in that protocol.

XIV. DOCUMENTATION

A. Instrument Log Books

Record information in the designated log book of the instrument being used for the analysis. Information must include method type, date and time of run, digestion groups being run, analyst's initials.

B. Standard Prep Log Book

Record the necessary information in the prep log book, including source, lot numbers, volumes utilized, date and time of prep and analyst's initials.

C. Maintenance Log Book

All maintenance performed will be documented and dated in the maintenance log.

D. Control Charts

Plot the % recovery of the LCS on the appropriate control chart. If an out-of-contol situation exists , record the corresponding nonconformance - corrective action number on the control chart.

E. Reporting

Waters are reported in ug/L and soils are reported in mg/Kg as received basis. The concentration results are reported to two significant figures. The reporting limits are listed in Table 1.

F. Data Review

After analysis, a peer or supervisor reviews the data and initials the log books and actual run.

XV. REFERENCES

A. USEPA Test Methods for Evaluating Solid Waste, SW846 third edition, November 1986, and updates - Method 6010A.

B. Perkin Elmer Plasma 40 and Thermo Jarrel Ash 61E instrument manuals.

TABLE 1

RECOMMENDED WAVELENGTHS AND ESTIMATED REPORTING LIMITS

Element	Estimated Wavelength(nm)	Reporting Limit (ug/L)
Aluminum	308.2	100
Antimony	206.83	60
Arsenic	193.70	100
Barium	455.40	100
Beryllium	313.04	5
Boron	249.77	100
Cadmium	228.80	5
Calcium	370.60	1000
Chromium	267.72	10
Cobalt	228.62	40
Copper	324.75	20
Iron	259.94	20
Lead	220.35	50
Magnesium	279.08	1000
Manganese	257.61	10
Molybdenum	202.03	30
Nickel	231.60	30
Potassium	766.49	1000
Selenium	196.03	100
Silicon	288.16	500
Silver	328.07	10
Sodium	588.99	1000
Thallium	190.86	100
Vanadium	292.40	50
Zinc	213.86	10

The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

TABLE 2

RUN SEQUENCE

1	ICV
2	ICB
3	LRS
4	ICSAI
5	ICSABI
6	PB
7	LCS
8	Sample 1
9	Sample 1D
10	Sample 1S
11	CCV
12	CCB
13	Sample 2
14	Sample 3
15	Sample 3L
16	Sample 4
17	Sample 5
18	Sample 6
19	Sample 7
20	Sample 8
21	ICSAF
22	ICSABF
23	CCV
24	CCB

TABLE 3

CALIBRATION STANDARD CONCENTRATION

ELEMENT	(S1) mg/L	(S2) mg/L	(S3) mg/L	(S4) mg/L	(S5) mg/L
Al	-	-	40.0	-	-
Sb	-	-	-	-	12.0
As	-	-	-	4.0	-
Ba	-	-	40.0	-	-
Be	-	-	1.0	-	-
Cd	-	-	-	2.0	-
Ca	100.0	-	-	-	-
Cr	-	2.0	-	-	-
Co	-	-	10.0	-	-
Cu	-	-	5.0	-	-
Fe	-	-	2.0	-	-
Pb	-	-	-	2.0	-
Mg	100.0	-	-	-	-
Mn	-	3.0	-	-	-
Mo	-	-	-	-	10.0
Ni	-	8.0	-	-	-
K	100.0	-	-	-	-
Ag	-	2.0	-	-	-
Na	100.0	-	-	-	-
Tl	-	-	-	4.0	-
V	-	-	10.0	-	-
Zn	-	4.0	-	-	-

TABLE 4

INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR ICP INTERFERENCE CHECK SAMPLE

Analytes	(mg/L)	Interferents	(mg/L)
Ag	1.0	Al	500
Ba	0.5	Ca	500
Be	0.5	Fe	200
Cd	1.0	Mg	500
Co	0.5		
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	1.0		
V	0.5		
Zn	1.0		

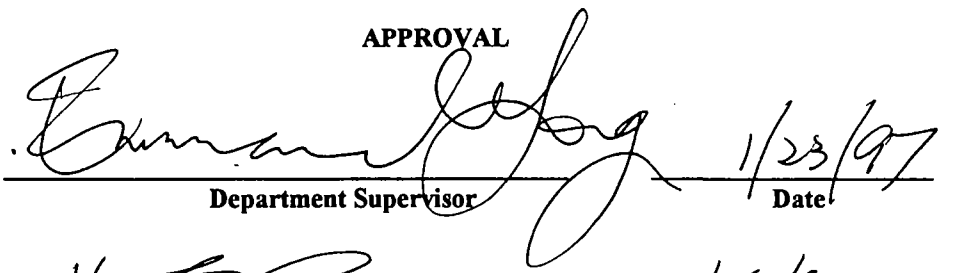
PACE ANLAYTICAL SERVICES, INCORPORATED
HOUSTON LABORATORY

STANDARD OPERATING PROCEDURE

Analysis
Polynuclear Aromatic Hydrocarbons in Water
(SW-846 Method 8310)

SOP NUMBER	**HO-O-027**
AUTHOR	**Russell Morgan**
Effective Date	**January 23, 1997**
Supersedes	**First Issue**

APPROVAL



Department Supervisor — **Date** 1/23/97

Quality Assurance Officer — **Date** 1/23/97

I. PURPOSE

This method is used to determine the concentration of certain polynuclear aromatic hydrocarbons (PAH) in water and waste.

II. SCOPE AND APPLICATION

A. This method provides high performance liquid chromatograph (HPLC) conditions for detecting certain polynuclear aromatic hydrocarbons in aqueous samples. Prior to analysis, samples are extracted using either separatory funnel or continuous liquid-liquid extraction techniques. A 20 mL aliquot of the extract is injected into a HPLC, and compounds in the HPLC effluent are detected by ultraviolet (UV) detector and/or fluorescence (FL) detectors. An aliquot of each matrix type must be spiked with spike recovery and the limits of detection.

B. The sensitivity of this method usually depends on the level of interference's rather than on instrumental limitations.

C. INTERFERENCE'S

1. Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of the chromatograms. All these materials must be demonstrated to be free from interference's under the conditions of the analysis by running method blanks.
2. Matrix interference will vary considerably from source to source.

III. RESPONSIBILITIES

A. PERSONNEL

1. All personnel involved with sample preparation and analysis are responsible for adherence to this SOP.
2. Personnel are responsible for ensuring that any deviations to this SOP are reported.
3. All personnel are responsible for notifying the laboratory manager and section supervisor of any required revisions to the SOP.

B. LABORATORY MANAGER/SECTION SUPERVISOR

1. The laboratory manager and section supervisor are responsible for ensuring a adherence to this SOP.
2. The laboratory manager and section supervisor are responsible for performing an annual review of the SOP and reporting any required revisions to the Quality Assurance Office.

C. QUALITY ASSURANCE OFFICE (QAO)

1. The QAO is responsible for conduction laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Management.
2. The QAO is responsible for ensuring that all revisions to the SOP are implemented .
3. The QAO is responsible for determining distribution of and maintaining document control for this SOP.

IV. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. At the time of review, any required revisions will be incorporated.

C. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

V. DISTRIBUTION

A. A controlled copy of this SOP will distributed to the following persons:
   1. Technician/Chemist performing sample preparation or analysis.
   2. Department supervisor

B. The original of this SOP will be retained by the QAO.

C. Distribution records will be retained by the QAO.

VI. GENERAL POLICIES/PROCEDURES

A. Compliant initial calibration for the analytes of concern is required before sample analysis may begin.

B. Continuing calibration standards must meet established method criteria before proceeding with sample analysis. If a calibration not specifically meeting the established method criteria is deemed acceptable by the section supervisor and is technically supported, sample analysis may proceed with client approval via the project manager. Because the calibration list of analytes may included "non-target" compounds, the calibration may be method compliant for all analytes of interest. Discrepancy reports must be completed and routed ad appropriate.

C. Quality Control results falling outside established acceptance criteria will be documented with scientific justification for acceptance of data or footnoted regarding reanalysis or re-extraction requirements. Supervisor approval is required before proceeding with analysis. Discrepancy reports must be completed and routed as appropriate.

VII. SAMPLE COLLECTION, PRESERVATION AND HANDLING

A. CONTAINERS
Containers used to collect samples are 1000mL glass.

B. STORAGE
The samples must be refrigerated at 1-4 C from the time of collection until extraction. The extracts must also be refrigerated until analysis.

C. HOLDING TIME LIMITS

All samples shall be analyzed as soon as possible upon receipt by the laboratory. The extraction holding time is 7 days from sampling for water samples and 14 days for waste or solid samples. The analysis holding time is 40 days from extraction.

VIII. PREPARATION PROCEDURES

A.

IX. INSTRUMENTAL ANALYSIS

A. Polynuclear aromatic hydrocarbons are to be analyzed on a HPLC equipped with an ultraviolet detector and a fluorescence detector according to the instrumental conditions described within this method.

X. CALIBRATION STANDARDS

A. Stock Standards

1. Calibration Standard Solution - 'Supelco' 610 M PAH mix or equivalent with sufficient traceability documentation. Refer to for final concentration.
2. Surrogate Stocks - Prepare stock solutions of p-Terphenyl (d14) and Carbazole by dissolving ca. 40 mg of carbazole in 10 mL acetonitrite (ACN) and 15 mg p-terphenyl (d14) in 25 mL methylene chloride ($MeCl_2$). Solutions of these two components can be added to a 10-mL volumetric to yield final concentrations of 50 mg/mL and 100 mg/mL for Carbazole and p-Terphenyl (d14) respectively in ACN. The stock solutions are transferred to amber crimp-top reagent bottles and stored at 1-4° C. These stock solutions may be used, provided sufficient traceability documentation is available.

B. Intermediary Solutions

1. Matrix Spike, Lab Control Spike - To a 10.0 mL volumetric flask, add 1.0 mL Supelco 610 M PAH mix or equivalent and 2.0 mL surrogate intermediate spiking solution and dilute to the mark with ACN.
2. Surrogate Standard Intermediary Spiking Solution - Make appropriate dilutions of the two stock solutions in a single 100 mL volumetric flask to yield concentrations of 10 mg/mL carbazole and 20 mg/mL p-terphenyl in ACN.
3. Surrogate Standard Intermediary Calibration Solution - Using the same stock solutions as in Section X.A.2, make appropriate dilutions in a single 10 mL volumetric flask to yield concentrations of 1.0 mg/mL carbazole and 2.0 mg/mL p-terphenyl in ACN.

C. Standard Solutions

1. Add 1.0 mL of X.A.1 and 2.0 mL of X.A.2 to a 10 mL volumetric flask. Dilute with ACN and mix. Individual analyte concentrations are summarized in. Label as "PAH St'd 6". (This is the stock solution for initial calibration standards preparation.)
2. Add 0.5 mL of X.C.2 (PAH St'd 6) to a 2 mL crimp top vial and bring to 1 mL with ACN. Individual analyte concentrations are summarized in. Label as "PAH St'd 5".
3. Add 300 uL of X.C.2 to a 2 mL crimp top vial and bring to 1 mL with ACN. Individual analyte concentrations are summarized in . Label as "PAH St'd 4".
4. Add 1.0 mL of X.C.2 to 10 mL volumetric flask and dilute to volume with ACN. Individual analyte concentrations are summarized in. Label as "PAH St'd 3".

5. Add 30 mL of X.C.2 to a 2 mL crimp top vial and bring to 1 mL with ACN. Individual analyte concentrations are summarized in . Label as "PAH St'd 2".
6. Add 10 mL of X.C.2 to a 2 mL crimp top vial and bring to 1 mL with ACN. Individual analyte concentrations are summarized in Table 2. Label as "PAH St'd 1".
7. Add 5 uL of X.C.2 to a 2 mL crimp top vial and bring to 1 mL with ACN. Label as "PAH IDL St'd".

D. *Continuing Calibration Check Solution* - PAH St'd 3 is used as the *Continuing Calibration* Check, as prepared in X.C.4.

E. External Calibration Check Standard. This standard should be prepared from a source other than that of the calibration standard stock solution. If a second course is not available, the standard should be prepared using a different lot of PAH mix. The level of this standard should be about the same as "PAH St'd 3".

XI. INITIAL INSTRUMENT CALIBRATION

A. Initial calibration requires the analysis of a solvent blank and the five calibration standards from X.C.2 through Section X.C.6. The blank is used to assure system integrity. The IDL standard is analyzed to assure sufficient sensitivity to support the reporting limit listed in Table 5.

B. The responses for the PAH St'd 1 through PAH St'd 5 are divided by the concentration for each compound and an average response factor is calculated for each analyte. The RSD (relative standard deviation, calculated as sample standard deviation divided by average response) for any compound must be $\leq$20%. One of the five concentrations should be near the method reporting limit. The other concentrations should correspond to the expected *linear range of the instrument.*

C. Following each initial calibration, an External Check Standard (X.E.) must be analyzed. The external check standard results, calculated from the average response factor from the initial calibration curve, must be within ±20% of the true value.

XII. DAILY CALIBRATION VERIFICATIONS

A. Before sample analysis each day, the continuing calibration standard is analyzed. This is PAH St'd 3 from section X.C.4. The response must fall within the required ±15% of the *true value of the standard, quantitated from the current acceptable initial calibration.* If the response fails this check, the daily standard is reanalyzed. If the response from the reanalysis does not meet the acceptance criteria, then initial calibration and/or instrument maintenance is repeated before samples are analyzed.

B. The continuing calibration standard is analyzed after every 10 samples throughout the analysis run. The response must be within ±15% of the true value of the standard, quantitated from the current initial calibration. If the response is not within the acceptance range, the daily standard is reanalyzed. If the response from the second analysis is not acceptable, the system is considered to have failed calibration. In this case, initial calibration *and/or instrument maintenance is performed and all samples analyzed since the* last acceptable continuing calibration standards are reanalyzed. All maintenance will be recorded in the log book.

C. After sample analyses are completed each day, the continuing calibration standard is reanalyzed. The response must be within ±15% of the true value of the standard quantitated from the current initial calibration. If the response is not within the acceptance range, the daily standard is reanalyzed. If the response from the second analysis is not acceptable, the system is considered to have failed calibration. In this case, initial calibration and/or instrument maintenance is performed and all samples analyzed since the last acceptable continuing calibration standards are reanalyzed. All maintenance will be recorded in the log book.

XIII. SAMPLE ANALYSIS

A. Reagents
1. Filter reagents (water, acetonitrile) through 0.45um filters
2. Use glass vacuum filter cone and glass flask
3. Return reagents to the 4-liter amber bottles and hook up to solvent lines
4. Solvent lines have 0.45 um filters attached to both sparge and reservoir lines
5. These lines run through a cap that protects solvents from dust
6. Water-solvent A; Acetonitrile-solvent B

B. Hardware
1. Turn on HPLC-wait for OK from instrument
2. Turn on Fluorescence detector
3. Turn on monitor, printer, and the cpu last

C. HPLC
1. Press the Setup menu-use arrow keys to move between options
2. Sparge solvents with pure helium at 100 ml/min. for at least 20 minutes
3. After 20 minutes set sparge flow rate to 20 ml/min; remains throughout the run
4. Set column temperature to 25 C
5. Both UV and Fluorescent lamp need at least one hour to warm up
6. Use syringe to remove air bubbles from each solvent line
   a. set solvent ratios to 100% A,0%B,0%C,0%D
   b. screw syringe onto valve; turn valve from "run" to "draw"
   c. Draw off approx. 10 mls
   d. Turn valve back to "run", unscrew syringe and discard in waste
   e. set solvent ratios to 0%A,100%B,0%C,0%D
   f. repeat steps b-e
7. Reset solvent proportions to 100%B, 0%A

D. HPLC Warm up
1. Press "Program Tables"
2. Go to (startup table) use arrow keys to maneuver there
   a. Table is set up to ramp flowrate from 0 to 1.6 ml/min of 100%B in 10 min.
   b. Then it changes ratios to 53%A:47%B in 15 min.
   c. Allows for gradual change in flowrate and solvent proportions
3. Save table 15; check corresponding tables and save each one as table 15
   a. There are 3 subtables that make up a table
   b. 1st table controls flowrates and solvent ratios
   c. 2nd table controls on/off timing of sparge, temp, lamp and triggers fluorescent detector at beginning of each cup
   d. 3rd table controls wavelength of UV detector; all are saved under #15
4. Press "Program Steps"
   a. Under first cup type 101 and hit enter (code for equilibrate)

b. For time type 25.00 (duration of table 15 warm up)
c. Under table # enter 15
d. Save program

5. Press "Program Run"
   a. Press button again
   b. Press "Start Run"- activates the table(s) saved in their order

This starts the warm up stage that conditions and equilibrates the system and column

E. Computer
1. Type "max" and enter at the prompt
2. Hit enter at the first question posed to user
3. Type "n" and enter in response to the second question; this gets us into the Maxima program
4. Using mouse go to "Load" button
5. Go to directory and pull up method (MDL*****)
6. Go to "develop method"
   a. Method is already set up for 2 detectors, 18 components, the retention times and retention time windows
   b. Alter sample queue for each run (stds and samples)
   c. Give each sample a unique name/code under which the chromatograph will be saved; link it to the method title
   d. Save the method under its own name using the date

F. Running Samples
1. Press "Program Tables"
   a. Go to table 1-programmed to run at 1.6 ml/min continuously
   b. Ramps solvent proportions from 53%A:47%B to 100%B linearly in 28 min.
   c. Runs on 100%B for another 17 min.- totals a 35 min. for each cup
   d. Then ramps solvents back to original proportions in 10 min.-45 min run
   e. Save table 1 and check corresponding tables-save each one under #1
2. Press "Program Steps"
   a. Enter first and last vial #_s, run time (45.00), sx aliquot (25 ul) and table # (1)
   b. Number of vials should equal those in sample queue
   c. Save program
3. Computer-go to "Execute Method"
   a. Hit "Run Samples"
   b. Verify the beginning of background acquisition
   c. Computer will say "Waiting for external trigger"
   d. Trigger sent by HPLC-preprogrammed in method
4. HPLC-press "Program Run"
   a. Press button again
   b. Press "Start Run"
   c. HPLC will rinse needle and inject the first sample-triggers the software and the Fluorescence detector with each vial-resets initial conditions of the Fluorescent detector for each vial.

G. Fluorescence Detector
1. Press "Monitor"
2. Enter 1 for program 1
3. Programmed to change wavelengths at certain times

4. Before a large run-send one sample through to verify retention times
   a. Pressure and temperature variations affect retention times
   b. Alter times of wavelength changes to reflect new conditions
   c. If not done then wavelength changes at the wrong time can affect peaks

H. Shut Down
1. Press "Program Tables"
2. Go to table 14
   a. Programmed to change solvents ratios to 100%B at 1.6 ml/min in 15 min
   b. Then ramps flowrate down to 0 ml/min in 10 min.
   c. Follow steps VI-1-e through VI.-4-b; use respective times and table #_s
3. Leaves the column in 100% Acetonitrile
4. Turn off cpu, monitor, printer, Fluorescence detector, and then HPLC
5. HPLC can be left on continuously if used often-then turn off lamp

XIV. QUANTITATION OF ANALYTES

A. Quantitation is performed on a target analyte only when the criteria in the sample analysis has been met.

B. The reporting limit of each analyte must be above the method detection limit established for each analyte. The reporting limit is a uniform detection level demonstrated by the lowest standard of the analyte. The reporting limits are listed in Table 5. If required by a specific QA plan, analytes can be reported with a "J" flag below the reporting limit but above the MDL.

C. The concentrations are calculated by the following equations.

Equation 1

$$Conc(ug/L) = \frac{(Cx)(Vt)}{V} x(Df)$$

where
- Cx = Concentration of the peak for the compound to be measured in the sample extract (ug/mL)
- Vt = Final volume of the sample extract in milliliters
- V = Initial volume of the sample in liters
- Df = Dilution factor

D. The recovery of the surrogates are calculated according to the following equation.

Equation 2

$$\% \ Recovery = \frac{Qd}{Qa} \ x100$$

where:
- Qd = Quantity determined by analysis
- Qa = Quantity added to the sample/blank (TV)

XV. BLANKS

A. A method blank must be extracted and analyzed with each set of samples. The method blank is used to check for background contamination. No more than 20 samples can be associated with a method blank.

B. The surrogate spiking requires concentration verification prior to use against a working calibration curve. Recoveries should be between 80 and 120%.

C. The method blank shall contain no known additions of target compounds except the two surrogate standards, p-terphenyl(d14) and carbazole. If target analytes are detected above the reporting limit, the method blank shall be reanalyzed. If upon reanalysis, method blank contamination is confirmed, the whole sample set will be suspect and should be reextracted and reanalyzed.

XVI. MATRIX SPIKE/MATRIX SPIKE DUPLICATE

A. Matrix Spike/Matrix Spike Duplicate (MS/MSD) samples are spiked in the same manner as the LCS/LCSD and processed as a sample along with other environmental samples. The MS/MSDs are used to determine the suitability of the method for a particular sample matrix. See Table 3 for acceptance limits.

B. The spiking standard requires concentration verification prior to use against a working calibration curve. Recoveries should be between 80 and 120% for all compounds.

C. The percent recoveries and the relative percent difference between the recoveries of each of the compounds in the MS and MSD will be calculated and reported using the following equation.

Equation 3

$$\%\ Recovery = \frac{MS\text{-}SR}{(1/2)(MSR = MSDR)}\ x100$$

D. The limits for matrix spike compounds recovery and RPD limits are listed in Table 3. Failure to meet these limits requires action by the laboratory and technical justification must be documented in order to accept an out of control data points.

XVIII. REFERENCES

A. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 3rd Edition and Update I. Method 8310 (Polynuclear Aromatic Hydrocarbons).

STANDARD OPERATING PROCEDURE

Total Phosphorus and Orthophosphate

SOP Number	HO-I-023-A
Author	Russell Morgan
Effective Date	July 8, 1993
Supersedes	First Issue

Approvals:

Bruce Bynum
General Chemistry Supervisor — 7-12-93 Date

Russell Lee Morgan
Inorganic Laboratory Manager — 7-10-93 Date

Quality Assurance Officer — 7-12-93 Date

I. PURPOSE

This SOP covers the determination of specified forms of phosphorus in drinking, surface and saline waters, and domestic and industrial wastes.

II. SCOPE

This SOP is based on reactions that are specific for the orthophosphate ion. Thus, dependant on the prescribed pre-treatment of the sample.

III. TEST RANGE

The methods are usable in the 0.01 to 1.0 mg/L range.

IV. RESPONSIBILITIES

A. Analysts

1. All analysts performing this procedure are responsible for strict adherence to the SOP.

2. Analysts are responsible for ensuring that any deviations to this SOP are reported.

3. Analysts are responsible for reporting to the section supervisor any required revisions to the SOP.

B. Department Supervisors/Managers

1. The department supervisor/manager is responsible for ensuring adherence to this SOP.

2. The department supervisor/manager is responsible for performing an annual review of this SOP and reporting any required revisions to the Quality Assurance Officer.

C. Quality Assurance Officer (QAO)

1. The QAO is responsible for conducting semi-annual laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Regional Management and Corporate Quality.

2. The QAO is responsible for ensuring that all revisions to the SOP are implemented

3. The QAO is responsible for determining distribution of and maintenance of document control for this SOP.

IV. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

V. DISTRIBUTION

This SOP will be issued to the Inorganic Chemistry Manager, the Section Supervisor, Corporate QAO, and any other areas deemed appropriate by the Regional QAO.

VI. INTERFERENCES

No interference is caused by copper, iron or silicate at concentrations many times greater than their reported concentration in sea water. However, high iron concentrations can cause precipitation of and subsequent loss of phosphorus.

VII. HAZARDS AND PRECAUTIONS

A. Wear lab coat and safety glasses with side shields at all times while performing this procedure. Wear gloves to avoid skin contact with possible toxicants contained in the samples for analysis.

1. Should skin or eye contact occur, flush the exposed area(s) with large amounts of water and seek immediate medical attention.

2. Never pipet materials by mouth. Use a rubber bulb or other approved suction device to transfer materials by pipet.

B. Handle and store all reagents in accordance with the precautions listed on the material safety data sheets (MSDSs).

1. Consult the MSDS for each reagent listed in this procedure before use. The MSDS will provide pertinent information on toxicity, safety precautions and storage conditions.

2. Always consult the label on the reagent bottle for up-to-date information on safety precautions during handling, preferred storage conditions, and expiration data.

3. Label all flasks, vials, etc. with the intended contents prior to filling. Follow established laboratory procedure in completing and affixing labeling information to equipment.

C. Handle all glass equipment with care, particularly during periods of heating and cooling.

VIII. APPARATUS AND MATERIALS

A. Photometer: A spectrophotometer or filter photometer suitable for measurements at 650 or 880 nm with a light path of 1 cm or longer.

B. Acid-Wash Glassware with 1:1 HCL, then triple rinse with DI water.

1. 1 - 50 ml graduated cylinder
2. 1 - 100 ml graduated cylinder
3. 5 - 100 ml volumetric flasks
4. 1 - 500 ml beaker
5. 125 ml acid-washed Erlenmeyer flasks
6. 125 ml acid-washed beakers (or plastic cups)

C. Reagents

1. Sulfuric acid solution, 5 N: Dilute 70 ml of concentrated H_2SO_4 with distilled water to 500 ml

2. Antimony potassium tartrate solution: Weigh 1.3715 g $K(SbO)C_4H_40_6 \cdot 1/2H_2O$. Dissolve in 400 mL distilled water in 500 mL volumetric flask; dilute to volume. Store at 4°C in a dark, glass-stoppered bottle.

3. Ammonium molybdate solution: Dissolve 20 g $(NH_4)\ 6Mo7O_24 \cdot 4H_4O$ in 500 mL of distilled water. Store in a plastic bottle at 4°C.

4. Ascorbic acid, 0.1 M: Dissolve 1.76 g of ascorbic acid in 100 mL of distilled water. The solution is stable for about a week if stored at 4°C.

5. Combined reagent: Mix the above reagents in the following proportions for 100 mL of the mixed reagent. 50 mL of 5N H_2SO_4, 5 mL of antimony potassium tartrate solution, 15 ml of ammonium molybdate solution, and 30 ml of ascorbic acid solution. Mix after addition of each reagent. All reagents must reach room temperature before they are mixed, and must be mixed in the order given. If turbidity forms in the combined reagent, shake and let stand for a few minutes until the turbidity disappears before proceeding. Since the stability of this solution is limited, it must be freshly prepared for each run.

6. Sulfuric acid solution, 11 N: Slowly add 310 mL concentrated H_2SO_4 to 600 mL distilled water. When cool, dilute to 1 L.

7. Ammonium persulfate.

8. 50 mg/L stock phosphorus standard: Dissolve in distilled water 0.2197 g of potassium dihydrogen phosphate, KH_2PO_4, which has been dried in an oven at 105°C. Dilute the solution to 1000 ml; 1.0 mL - 0.05 mg P.

9. 50 mg/L ICV phosphorus standard: Dissolve in distilled water 0.2197 g of potassium dihydrogen phosphate, KH_2PO_4 from a separate source, which has been dried in an oven at 105°C. Dilute the solution to 1000 ml; 1.0 mL - 0.05 mg P.D

IX. PROCEDURE

A. Total Phosphorus

1. Add 1 mL of the 11 N H_2SO_4 solution to a 50 mL sample in a 125 mL Erlenmeyer flask.

2. Add 0.4 g of ammonium persulfate.

3. Heat for 30 minutes in an autoclave at 121°C (15-20 psi)

Autoclave:

a. Put sample in tray and make sure drain is on "close"
b. Fill with DI to lower ledge, close door and set timer for 30 minutes
c. Don't open until temperature is below 120°C or until pressure is @ 0 (be careful of steam)
d. Open drain
e. Let sample cool
f. Use acid-washed funnels and filter with 41 15.1 cm filter paper, if needed
g. Filter if solid chunks are present

B. Orthophosphate

1. The pH of the sample must be adjusted to 7 ± 0.2 using a pH meter.

2. To adjust pH, add 2 drops of phenophalien indicator and 1.0 ml of 10 N NaOH and swirl around. Add 2 N NaOH dropwise until pink, then 5 N sulfuric acid dropwise until clear.

C. Calibration

1. Use 25 ml of the following standards brought up to 40 ml final volume.

a. Blank = 40 mL of DI water and zero instrument
b. Midrange (0.5 mg/L) = 1.0 ml of 50 mg/l as P to 100 ml volume
c. DL (0.01 mg/L) = 2.0 ml of midrange standard to 100 ml volume

d. High (1.0 mg/L) = 2.0 ml of 50 mg/l as P to 100 ml volume
e. ICV (0.5 mg/L) = 1.0 ml of 50 mg/l as P to 100 ml volume (separate source)

D. Color Development

1. Total Phosphorus

a. Bring pH-adjusted sample to 80 ml final volume in a graduated cylinder, then divide into 2 - 40 ml color aliquots. Use one aliquot for the initial color reading and then use the second in case any dilutions are required. All dilutions will be made to a 40 ml color aliquot.

b. Add 4.0 ml of combined reagent to sample and mix thoroughly. After a minimum of ten minutes, but no longer than thirty minutes, measure the color absorbance of each sample at 880 mm with a spectrophotometer, using the reagent blank as the reference solution.

2. Orthophosphate

a. Add 4.0 ml of combined reagent to 25 ml of sample brought to 40 ml; mix thoroughly. After a minimum of ten minutes, but no longer than thirty minutes, measure the color absorbance of each sample at 880 mm with a spectrophotometer, using the reagent blank as the reference solution.

E. Calculations

Determine mg/L of phosphorus as P using linear regression on the three calibration points. The correlation coefficient must be ≥ 0.998. Multiply by any color dilution factor for final results.

X. QUALITY CONTROL

A. Method Blanks

50 ml DI water taken through entire procedure for each batch of 20 samples.

B. LCS (0.5 mg/L): Add 0.5 ml of 50 mg/L as P standard to 50 ml DI and take through the entire procedure for each batch of 20 samples.

C. Calibration (Reagent) Blank

D. Calibration Standards

1. Detection Limit (DL) Standard = 0.01 mg/L as P
2. Midrange Standard = 0.5 mg/L as P
3. High Range Standard = 1.0 mg/L as P

D. ICV Standard: 0.5 mg/L as P (separate source from calibrants)

E. Midrange Standard: Continuing Calibration Verification (CCV) standard (0.5 mg/L as P) must be done every 10 samples. Acceptance = ± 10%

F. A CCB must be done every 10 samples. Acceptance = <0.01 mg/L

XI. REFERENCES

A. EPA Methods for the Chemical Analysis of Water and Waste, March 1983, Method 365.2

STANDARD OPERATING PROCEDURE

Total and Amenable Cyanide in Water and Soil SW 846, Method 9010

SOP Number:	HO-I-037-A
Author:	Bruce Brown
Effective Date:	May 1, 1993
Supersedes:	First Issue

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Approvals:

Bruce Brown
General Chemistry Supervisor

7-23-93
Date

Russell Lee Maya
Inorganic Laboratory Manager

7/23/93
Date

for Kevin Anders
Quality Assurance Officer

7/26/93
Date

I. PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to establish a procedure for the determination of total and amenable cyanide for SW846 Method 9010.

II. SCOPE/APPLICATION

Method 9010 is used to determine the concentration of inorganic cyanide in an aqueous waste or leachate. The method detects inorganic cyanides that are present as either simple soluble salts or complex radicals. It is used to determine values for both total cyanide and cyanide amenable to chlorination. Method 9010 is not intended to determine if a waste is hazardous by the characteristic of reactivity.

III. SAFETY INFORMATION

A. Standard laboratory safety practices must be followed.

B. Color reagents should be added and mixed beneath a fume hood due to the possible generation of toxic cyanogen chloride.

C. Analyte information: Cyanide is assigned in the Chemical Abstract Registry (CAS) Number 57-12-5.

IV. SUMMARY OF METHOD

A. The cyanide, as hydrocyanic acid (HCN), is released by refluxing the sample with strong acid and distillation of the HCN into an absorber-scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then manually determined colorimetrically.

B. In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The concentration of NaOH must be the same in the standards, the scrubber solutions, and any dilutions of the original scrubber solution to obtain colors of comparable intensity.

V. RESPONSIBILITIES

A. QUALITY ASSURANCE OFFICER

1. The Quality Assurance Officer (QAO) has overall responsibility for monitoring implementation of and adherence to the policies and procedures set forth in this document.

2. The QAO will conduct semi-annual audits of the facility to monitor adherence to this and other SoPs. The results of the audit will be reported to Regional Management and Corporate Quality.

B. INORGANIC MANAGER / SUPERVISOR

1. The Manager/Supervisor has responsibility to ensure adherence to this SOP.

2. The Manager/Supervisor will ensure that this SOP is reviewed on an annual basis.

3. The Manager/Supervisor will ensure that the QAO is notified when revisions to the SOP are required.

C. ANALYST

1. The analyst is responsible for following all procedures set forth in this document. The analyst will report any deviations to the procedures set forth in this document.

2. The analyst is responsible for reviewing the SOP on an annual basis and reporting any required revisions to the department manager or supervisor.

VI. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. At the time of review, any required revisions will be incorporated and the superseded document replaced

VII. DISTRIBUTION

A. Distribution of this SOP will be determined by the Quality Assurance Officer.

B. Distribution records will be maintained by the Quality Assurance Officer.

VIII. SAMPLE COLLECTION, PRESERVATION AND HANDLING

A. All samples must have been collected using a sampling plan.

B, Samples should be collected in 1 liter, or larger, plastic or glass bottles. All bottles must be thoroughly cleaned and thoroughly rinsed to remove soluble materials from containers.

C. Oxidizing agents, such as chlorine, decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with acidified potassium iodide (KI)-starch test paper as soon as the sample is collected; a blue color indicates the need for treatment. Add ascorbic acid a few crystals at a time until a drop of sample produces no color on the indicator. Then add an additional 0.6 g of ascorbic acid for each liter of water.

D. Samples must be preserved by addition of 10 N sodium hydroxide until sample pH is greater than or equal to 12 at the time of collection.

E. Samples should be refrigerated at 4°C, when possible, and analyzed as soon as possible.

IX. INTERFERENCES

A. Interferences are eliminated or reduced by procedures described in paragraph XII.B.3, 4 and 5.

B. Sulfides adversely affect the colorimetric procedures. Samples that contain hydrogen sulfide, metal sulfides or other compounds that may produce hydrogen sulfide during the distillation should be treated by the addition of bismuth nitrate prior to distillation as described in paragraph XII.B.3.

C. High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds, once formed, will decompose under test conditions to generate HCN. The possibility of interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

X. APPARATUS AND MATERIALS

A. Reflux distillation apparatus: Shown in Figure 1 or 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber is a Fisher-Milligan scrubber (Fisher Catalog #07-513) or equivalent.

B. Spectrophotometer: Suitable for measurements at 578 nm with a 1.0 cm cell or larger.

C. Potassium iodide starch test paper.

XI. REAGENTS

A. ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

B. Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in Type II water, and dilute to 1 liter with Type II water.

C. Bismuth nitrate solution: Dissolve 30.0 grams of $Bi(NO_3)_3$ in 100 mL of Type II water. While stirring, add 250 mL of glacial acetic acid. Stir until dissolved. Dilute to 1 liter with Type II water.

D. Sulfuric acid, 1:1: Slowly add 500 mL of concentrated H_2SO_4 to 500 mL of Type II water.

Caution: This is an exothermic reaction.

E. Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 liter of Type II water.

F. Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of Type II water. Standardize with 0.0192 N $AgNO_3$. Dilute to appropriate concentration so that 1 mL equals 1 mg CN.

G. Intermediate standard cyanide solution: Dilute 100.0 mL of stock cyanide solution (1 mL = 1 mg CN) to 1,000 mL with Type II water (m mL = 100 ug CN)

H. Working standard cyanide solution: Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1,000 mL with Type II water (1 mL = 10.0 ug CN). Store in a glass-stoppered bottle.

I. Magnesium chloride solution: Weigh 150 g of $MgCl_2 \cdot 6H_2O$ into a 1,000 mL flask, dissolve, and dilute to 1 liter with Type II water.

J. Sulfamic acid solution: Dissolve 40 g sulfamic acid in Type II water. Dilute to 1 liter.

K. Calcium hypochlorite solution: Dissolve 5 g of calcium hypochlorite [$Ca(OCl)_2$] in 100 mL of Type II water.

L. Reagents for manual colorimetric determination:

1. Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250-mL volumetric flask, add just enough Type II water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of concentrated HCl, mix and cool to room temperature. Dilute to 250 mL with Type II water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

2. Chloramine-T solution: Dissolve 1.0 g of white, water-soluble chloramine-T in 100 mL of Type II water and refrigerate until ready to use.

M. Ascorbic acid: Crystals

N. Phosphate buffer, pH 5.2: Dissolve 13.6 g of potassium dihydrogen phosphate and 0.28 g of disodium phosphate in 90 mL of Type II water, and dilute to 1 liter.

XII. PROCEDURE

A. Pretreatment for Cyanides Amenable to Chlorination

1. Two sample aliquots are required to determine cyanides amenable to chlorination. To one 500 mL aliquot, or to a volume diluted to 500 mL, add calcium hypochlorite solution (paragraph XI.K) dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide solution (paragraph XI.B).

   Caution: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is recommended that this reaction be performed in a hood. For convenience, the sample may be agitated in a 1 liter beaker by means of a magnetic stirring device.

2. Test for residual chlorine with KI-starch paper (paragraph X.C) and maintain this excess for 1 hour, continuing agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional hypochlorite solution.

3. After 1 hour, add 0.5 g portions of ascorbic acid until KI-starch paper shows no residual chlorine. Add an additional 0.5 g of ascorbic acid to ensure the presence of excess reducing agent.

4. Test for total cyanide in both the chlorinated and unchlorinated aliquots. (The difference of total cyanide in the chlorinated and unchlorinated aliquots is the cyanide amenable to chlorination.)

B. Distillation Procedure

1. Place 500 mL of sample, or an aliquot diluted to 500 mL in the 1 liter boiling flask. Pipet 50 mL of sodium hydroxide solution (paragraph XI.B) into the absorbing tube. If the appratus in Figure 1 is used, add Type II water until the spiral is covered. Connect the boiling flask, condenser, absorber and trap in the train (Figure 1 or 2).

2. Through the air inlet tube, start a slow stream of air entering the boiling flask by adjusting the vacuum source. Approximately two bubbles of air per second should enter the boiling flask.

3. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper. If positive, treat the sample by adding 50 mL of bismuth nitrate solution (paragraph XI.C) through the air inlet tube after the air rate is set. Mix for 3 minutes prior to addition of H_2SO_4.

4. If samples are suspected to contain NO_3 and/or NO_2, add 50 mL of sulfamic acid solution (paragraph IX.J) after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of H_2SO_4.

5. Slowly add 50 mL 1:1 H_2SO_4 (paragraph XI.D) through the air inlet tube. Rinse the tube with Type II water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride (paragraph XI.I) into the air inlet and wash down with the stream of water.

6. Heat the solution to boiling. Reflux for 1 hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

7. Drain the solution from the absorber into a 250 mL volumetric flask. Wash the absorber with Type II water and add the washings to the flask. Dilute to the mark with Type II water.

C. Manual Spectrophotometric Determination

1. Withdraw 50 mL or a measured lesser amount of the solution from the flask and transfer to a 100 mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25 N sodium hydroxide solution (paragraph XI.B). Add 15.0 mL of sodium dihydrogenphosphate solution (paragraph XI.E) and mix.

2. Add 2 mL of chloramine-T (paragraph XI.L.2) and mix. See note immediately following. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (paragraph XI.L.1) and mix. Dilute to mark with

Type II water and mix again. Allow 8 minutes for color development and then read absorbance of 578 nm in a 1 cm cell within 15 minutes.

Note: Some distillates may contain compounds that have a chlorine demand. One minute after the addition of chloramine-T, test for residual chlorine with KI-starch paper. If the test is negative, add an additional 0.5 mL chloramine-T. Recheck after 1 minute.

D. Standard Curve for Samples Without Sulfide

1. Prepare a series of standards by pipetting suitable volumes of working standard potassium cyanide solution into 250 mL volumetric flasks. To each flask, add 50 mL of 1.25N sodium hydroxide and dilute to 250 mL with water. Prepare using the following table. The sodium hydroxide concentration will be 0.25N.

mL of Working Standard Solution (1 mL = 10 μg CN^-)	Concentration (μg CN^-/L)
0	Blank
0.5	20
1.0	40
2.0	80
5.0	200
10.0	400
15.0	600
20.0	800

2. After the standard solutions have been prepared according to the table above, pipet 50 mL of each standard solution into a 100 mL volumetric flask and proceed to paragraph XII.C to obtain absorbance values for the standard curve. The final concentrations for the standard curve will be one half of the amounts in the above table (final concentrations ranging from 10 to 400 μg/L).

3. It is recommended that a mid range lab control standard (LCS) be distilled and compared to similar values on the curve to ensure that the distillation

technique is reliable. If the distilled standard does not agree within the established control limits, the analyst should find the cause of the apparent error before proceeding.

4. Prepare a standard curve ranging from 10 to 400 µg/L by plotting absorbance of standard versus the cyanide concentration, or ny using linear regression on a calculator.

E. Standard Curve for Samples with Sulfide

1. It is imperative that all standards be distilled in the same manner as the samples using the method of standard additions. Standards distilled by this method will give a linear curve at low concentrations, but as the concentration increases, the recovery decreases. It is recommended that at least five standards be distilled.

2. Prepare a series of standards similar in concentration to those mentioned in paragraph XII.D.1 and analyze as in paragraph XII.C. Prepare a standard curve by plotting absorbance of standard versus the cyanide concentration.

F. Calculation: If the spectrophotometric procedure is used, calculate the cyanide, in µg/L, in the original sample as follows:

$$CN^- \ (\mu g/L) = \frac{A \times B \times C}{D \times E}$$

Where:

A = µg/L CN^- read from standard curve
B = mL of sample after preparation of colorimetric analysis (100 mL recommended)
C = *mL of sample after distillation (250 mL recommended)*
D = mL of original sample for distillation (500 mL recommended).
E = mL used for colorimetric analysis (50 mL recommended).

XIII. QUALITY CONTROL

A. Verify the calibration curve with an independent calibration verification standard (ICV). If the standards are not within 10% of the expected value, a new calibration curve is required. Verify the calibration curve with every sample batch of 10 by analyzing a mid-range continuing calibration verification (CCV) standard.

B. A duplicate and a matrix spike should be prepared every 10 samples to check the efficiency of sample distillation. Prepare a matrix spike by adding cyanide from the working standard or intermediate standard to 500 mL of sample to ensure a concentration of approximately 40 μg/L. The duplicate and matrix spike are brought through the entire sample preparation and analytical process.

C. The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences such as samples which contain sulfides.

XIV. METHOD PERFORMANCE

A. The titration procedure using silver nitrate is used for measuring concentrations of cyanide exceeding 0.1 mg/L. The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

B. EPA Method 335.2 (sample distillation with titration) reports that in a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.06 to 0.62 mg/L CN^-, the standard deviations for precision were $\pm$ 0.005 to $\pm$ 0.094, respectively. In a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/L CN^-, recoveries (accuracy) were 85% and 102%, respectively.

C. In two additional studies using surface water, ground water and landfill leachate samples, the titration procedure was further evaluated. The concentration range used in these studies was 0.5 to 10 mg/L cyanide. The detection limit was found to be 0.2 mg/L for both total and amenable cyanide determinations. The precision (CV) was 6.9 and 2.6 for total cyanide determinations and 18.6 and 9.1 for amenable cyanide determinations. The mean recoveries were 94% and 98.9% for total cyanide, and 86.7% and 97.4% for amenable cyanide.

XV. DOCUMENTATION

A. All instrument maintenance performed will be documented and dated in the maintenance log.

B. All analyses performed will be documented and dated in the analysis log book.

C. All reagents made to perform the analyses will be documented and dated with all quantities, manufacturers and lot numbers recorded in the reagent log book.

XVI. REFERENCE

SW846 Methods 9010 and 9010A

FIGURE 1

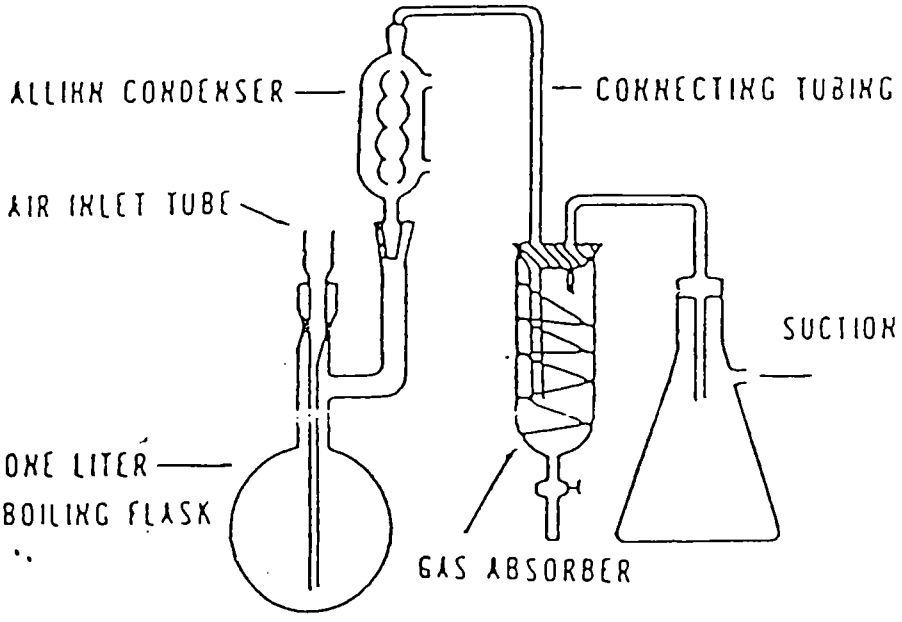
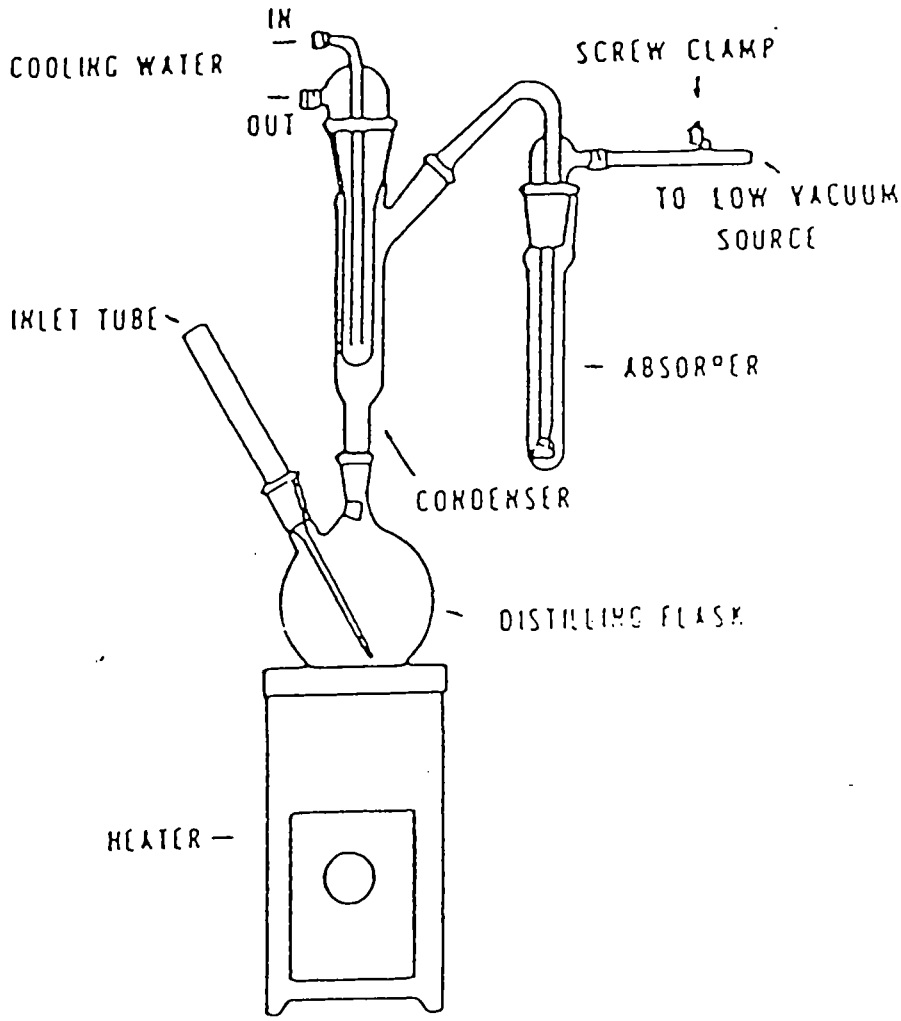

ALLIHN CONDENSER
CONNECTING TUBING
AIR INLET TUBE
SUCTION
ONE LITER
BOILING FLASK
GAS ABSORBER

FIGURE 2


IN
COOLING WATER
OUT
SCREW CLAMP
TO LOW VACUUM SOURCE
INLET TUBE
ABSORBER
CONDENSER
DISTILLING FLASK
HEATER

STANDARD OPERATING PROCEDURE

Fluoride by Ion Selective Electrode

SOP Number	HO-I-013-A
Author	Bruce Brown
Effective Date	January 14, 1997
Supersedes	First Issue

Approvals:

Bruce Brown 1/23/97

General Chemistry Supervisor Date

1/23/97

Quality Assurance Officer Date

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General Chemistry Supervisor Date

Inorganic Laboratory Manager Date

Quality Assurance Officer Date

STANDARD OPERATING PROCEDURE

Fluoride by Ion Selective Electrode

SOP Number HO-I-013-A

Effective Date: January 14, 1997

I. PURPOSE

A. This method is applicable to the measurement of fluoride in drinking, surface and saline waters, domestic and industrial wastes.

B. Concentration of fluoride from 0.1 up to 1000 mg/L may be measured.

C. For Total or Total Dissolved Fluoride, the Bellack distillation is required for NPDES monitoring but is not required for SDWA monitoring.

II. SUMMARY OF METHODS

The fluoride is determined potentiometrically using a fluoride combination electrode, and a pH meter having an expanded millivolt scale or a selective ion meter having a direct concentration scale for fluoride.

III. INTERFERENCES

Extremes of pH interfere; sample pH should be between 5 and 9. Polyvalent cations of Si+4, Fe+3 and Al+3 interfere by forming complexes with fluoride. The degree of interference depends on the concentration of the complexing cations, the concentration of fluoride and the pH of the sample. The addition of pH 5.0 buffer containing a strong chelating agent preferentially complexes aluminum (the most common interference), silicon and iron and eliminates the pH problem.

IV. RESPONSIBILITIES

A. Analytes

1. All analysts performing this procedure are responsible for strict adherence to the SOP.

2. Analysts are responsible for ensuring that any deviations to this SOP are reported.

3. Analysts are responsible for reporting to the section supervisor any required revisions to the SOP.

B. Department Supervisors/Managers

1. The department supervisor/manager is responsible for ensuring adherence to this SOP.

2. The department supervisor/manager is responsible for performing an annual review of this SOP and reporting any required revisions to the Quality Assurance Officer.

C. Quality Assurance Officer (QAO)

1. The QAO is responsible for conducting semi-annual laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Regional Management and Corporate Quality.

2. The QAO is responsible for ensuring that all revisions to the SOP are implemented.

3. The QAO is responsible for determining distribution of and maintenance of document control for this SOP.

V. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

VI. DISTRIBUTION

This SOP will be issued to the Inorganic Chemistry Manager, the Section Supervisor, Corporate QAO, and any other areas deemed appropriate by the Regional QAO.

VII. HAZARDS AND PRECAUTIONS

Each chemical compound used in this SOP should be treated as a potential health hazard. Care should be used while handling samples because of toxicity. Exposure to these substances must be reduced to the lowest possible level by whatever means available. (i.e. gloves, lab coats, eye protection, fume hoods). Reference files of OSHA regulations and Material Safety Data Sheets (MSDSs) are available to all personnel involved in this analysis.

VIII. SAMPLE HANDLING AND PRESERVATION

Use unpreserved bottles.

IX. APPARATUS

A. Electrometer (pH meter), with expanded mv scale, or a selective ion meter such as the Orion 400 Series.

B. Fluoride Ion Activity Electrode

C. Magnetic Mixer, Teflon©-coated stirring bar.

X. REAGENTS

A. Buffer solution, pH 5.0-5.5: To approximately 500 mL of distilled water in a 1 liter beaker, add 57 mL of glacial acetic acid, 58 g of sodium chloride and 4 g of CDTA (2). Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5 N sodium hydroxide (about 150 mL will be required). Transfer solution to a 1 liter volumetric flack and dilute to the mark with distilled water. For work with brines, additional NaCl should be added to raise the chloride level to twice the highest expected level of chloride in the sample.

B. Sodium fluoride, stock solution: 100 mg/L F. Dissolve 0.2210g of sodium fluoride in distilled water and dilute to 1 liter in a volumetric flask. Store in chemical-resistant glass or polyethylene.

C. Potassium fluoride stock ICV solution: 100 mg/L F. Dissolve 0.4955g of potassium fluoride $KF \cdot 2H_2O$ in distilled water and dilute to 1 liter in a volumetric flask. Store in chemical-resistant glass or polyethylene.

D. 10 mg/L High Range Standard: Add 10.0 mL of the 100 mg/L sodium fluoride stock solution to a 100 mL volumetric flask and bring to volume.

E. 1.0 mg/L Mid Range Standard: Add 10.0 mL of the 10 mg/L high range standard to a 100 mL volumetric flask and bring to volume.

F. 0.1 mg/L Detection Limit Standard: Add 10.0 mL of the 1.0 mg/L mid range standard to a 100 mL volumetric flask and bring to volume.

G. 5.0 mg/L ICV Standard: Add 5.0 mL of the 100 mg/L potassium fluoride stock ICV solution to a 100 mL volumetric flask.

H. Electrode Handling: The combination electrode should be stored in 100 mg/L fluoride solution when not in use. It should soak in DI water approximately 30 minutes prior to use.

XI. CALIBRATION

A. Begin calibration with the electrometer cleared and set on "conc." Add 25 mL of the 10 mg/L standard plus 25 mL of the buffer solution in a 100 mL beaker and immerse the electrode while stirring. After a couple of minutes, when the millivolt reading has stabilized, record the reading and press "set concentration".

B. Add 25 mL of the 1.0 mg/L standard plus 25 mL of the buffer solution to a 100 mL beaker and immerse the electrode while stirring. When the reading is stable, set the slope dials so that the instrument reads 1.0 mg/L. Record the slope setting.

C. Add 25 mL of DI water plus 25 mL of the buffer solution to a 100 mL beaker and immerse the electrode while stirring. When the reading is stable, press "set blank".

D. Read another 1.0 mg/L standard as in Step 2, and verify that the instrument reads ±10% of the Theoretical Value.

E. Add 25 mL of the 5.0 mg/L ICV standard plus 25 mL of the buffer solution to a 100 mL beaker and immerse the electrode while stirring. Allow the instrument to stabilize and record the reading. Verify that the reading is ±10% of the Theoretical Value.

XII. PROCEDURE

Place 25.0 mL of sample or standard solution and 25.0 mL of buffer in a 100 mL beaker. Place on a magnetic stirrer and mix at medium speed. Immerse the electrodes in the solution and observe the meter reading while mixing. The electrodes must remain in the solution for at least three minutes or until the reading has stabilized. At concentrations under 0.5 mg/L F, it may require as long as five minutes to reach a stable meter reading; high concentrations stabilize more quickly. If a pH meter is used, record the potential measurement for each unknown sample and convert the potential reading to the fluoride ion concentration of the unknown using the standard curve. If a selective ion meter is used, read the fluoride level in the unknown sample directly in mg/L on the fluoride scale.

Note: For industrial waste samples, this amount of buffer may not be adequate. Analysts should check pH first. If highly basic (>9), add 1 N HCI to adjust pH to 8.3.

XIII. QUALITY CONTROL

A. Matrix Spikes and Duplicates

1. For each day or every batch of 10 samples (whichever is most frequent) of similar matrix, one spike sample must be analyzed. Acceptable recovery limit is ±25%.

2. For every day or every batch of 10 samples (whichever is most frequent) of similar matrix, one sample must be prepared and analyzed in duplicate. Acceptable relate percent difference is <20%.

3. If range or RPD exceeds the limits for an aqueous sample matrix, reanalyze the duplicates and 25% of the positive samples in the batch, at a minimum.

B. Continuing Calibration Verification (CCV) Standard: One midrange standard must be analyzed every 10 samples. Acceptance limits are ±10% of Theoretical Value.

C. Continuing Calibration Blank (CCB): One blank must be analyzed every 10 samples. The acceptance limit is <0.1 mg/L.

XIV. REFERENCES

A. CDTA is the abbreviated designation of 1,2-cyclohexylene dinitrilo tetraacetic acid. (The monohydrate form may also be used.) Eastman Kodak 15411, Mallinckrodt 2357, Sigma D 1383, Tridom-Fluka 32869-32870 or equivalent.

B. Standard Methods for the Examination of Water and Wastewater, p 389, Method No. 414A, Preliminary Distillation Step (Bellack), and p 391, Method No. 414B, Electrode Method, 17th Edition, (1975).

C. Annual Book of ASTM Standards, Part 31, "Water", Standard D1179-72, Method B, p 312 (1976).

D. EPA Methods for the Chemical Analysis of Water and Wastewater, Method 340.2

STANDARD OPERATING PROCEDURE

Sulfate Turbidimetric

SOP Number	HO-I-015-C
Author	Bruce Brown
Effective Date	January 14, 1997
Supersedes	HO-I-015-B

Approvals:

Bruce Brown 1/23/97

General Chemistry Supervisor Date

1/23/97

Quality Assurance Officer Date

I. PURPOSE

II. SCOPE AND APPLICATION

A. This method is applicable to drinking, surface and saline waters, domestic and industrial wastes.

B. The method is suitable for all concentration ranges of sulfate; however, in order to obtain reliable readings, use a sample aliquot containing not more than 40 mg SO_4 L.

C. The minimum detectable limit is 2 mg/L sulfate.

III. SUMMARY OF METHODS

Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a nephelometer, filter photometer or spectrophotometer and compared to a curve prepared from standard sulfate solutions.

IV. RESPONSIBILITIES

A. Analytes

1. All analysts performing this procedure are responsible for strict adherence to the SOP.

2. Analysts are responsible for ensuring that any deviations to this SOP are reported.

3. Analysts are responsible for reporting to the section supervisor any required revisions to the SOP.

B. Department Supervisors/Managers

1. The department supervisor/manager is responsible for ensuring adherence to this SOP.

2. The department supervisor/manager is responsible for performing an annual review of this SOP and reporting any required revisions to the Quality Assurance Officer.

C. Quality Assurance Officer (QAO)

1. The QAO is responsible for conducting semi-annual laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Regional Management and Corporate Quality.

2. The QAO is responsible for ensuring that all revisions to the SOP are implemented.

3. The QAO is responsible for determining distribution of and maintenance of document control for this SOP.

V. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

VI. DISTRIBUTION

This SOP will be issued to the Inorganic Chemistry Manager, the Section Supervisor, Corporate QAO, and any other areas deemed appropriate by the Regional QAO.

VII. INTERFERENCES

A. Suspended matter and color interfere. Correct by running blanks from which the barium chloride has been omitted.

B. Silica in concentrations over 500 mg/l will interfere.

VIII. HAZARDS AND PRECAUTIONS

A. Wear lab coat and safety glasses with side shields at all times while performing this procedure. Wear gloves to avoid skin contact with the reagents.

1. Should skin or eye contact occur, flush the exposed area(s) with large amounts of water and seek immediate medical attention.

2. Never pipet materials by mouth. Use a rubber bulb or other approved suction device to transfer materials by pipet.

B. Handle and store all reagents in accordance with the precautions listed on the Material Safety Data Sheets (MSDSs).

1. Consult the MSDS for each reagent listed in this procedure before use. The MSDS will provide pertinent information on toxicity, safety precautions and storage conditions.

2. Always consult the label on the reagent bottle for up-to-date information on safety precautions during handling, preferred storage conditions, and expiration data.

3. Label all flasks, vials, etc. with the intended contents prior to filling. Follow established laboratory procedure in completing and affixing labeling information to equipment.

C. Handle all glass equipment with care, particularly during periods of heating and cooling.

IX. APPARATUS AND MATERIALS

A. Magnetic stirrer with variable speed so that it can be held constant just below splashing. Use magnetic stirring bars identical in shape and size.

B. Photometer: One of the following which are given in order of preference:

1. Spectrophotometer for use at 420 nm with light path of 4 to 5 cm.

2. Filter photometer with a violet filter having a maximum near 420 nm and a light path of 1 cm.

3. Stopwatch, if the magnetic stirrer is not equipped with an accurate timer.

4. Measuring spoon with capacity of 0.2 to 0.3 mL.

C. Reagents

1. Conditioning reagent: Place 30 mL concentrated HCI, 300 mL distilled water, 100 mL 95% ethanol or isopropanol and 75 g NACI in solution in a container. Add 50 mL glycerol and mix.

2. Barium chloride, $BaCl_2$, crystals, 20 to 30 mesh.

D. Standards

1. 1000 mg/L Stock Calibration Standard: Dissolved 1.479 g of anhydrous Na_2SO_4 in distilled water in a 1 liter volumetric flask and dilute to the mark with distilled water.

2. 1000 mg/L Stock ICV Standard: Dissolve 1.479g of anhydrous Na_2SO_4 (from a different source than the calibration standard) in distilled water in a 1 liter volumetric flask and dilute to the mark with distilled water.

3. 2.0 mg/L Detection Limit Standard: Add 0.2 ml of the 1000 mg/l stock calibration standard to DI water in a 100 ml volumetric flask and bring to the mark.

4. 5 mg/L Calibration Standard: Add 0.5 ml of the 1000 mg/L stock calibration standard to DI water in a 100 ml volumetric flask and bring to the mark.

5. 10 mg/L Calibration Standard: Add 1.0 of the 1000 mg/l stock calibration standard to DI water in a 100 ml volumetric flask and bring to the mark.

6. 20 mg/L Calibration Standard: Add 2.0 ml of the 1000 mg/L stock calibration standard to DI water in a 100 ml volumetric flask and bring to the mark.

7. 30 mg/L Calibration Standard: Add 3.0 ml of the 1000 mg/L stock calibration standard to DI water in a 100 ml volumetric flask and bring to the mark.

8. 40 mg/L Calibration Standard: Add 4.0 ml of the 1000 mg/L stock calibration standard to DI water in a 100 ml volumetric flask and bring to the mark.

9. 20 mg/L ICV Standard: Add 2.0 ml of the 1000 mg/L stock ICV standard to DI water in a 100 ml volumetric flask and bring to the mark.

X. SAMPLE HANDLING AND STORAGE

A. Samples are collected in unpreserved 1000 mL glass or plastic containers.

B. The samples must be refrigerated at approximately 4°C ± 2°C from the time of sample collection.

XI. PROCEDURE

A. Formation of barium sulfate turbidity.

1. Place 100 mL sample, or a suitable portion diluted to 100 ml, into a 250 Erlenmeyer flask.

2. Add exactly 5.0 mL conditioning reagent, then mix with the stirring apparatus.

3. While the solution is being stirred, add a measuring spoonful of $BaCl_2$ crystals and begin timing immediately.

4. Stir exactly 1 minute at constant speed.

B. Measurement of barium sulfate turbidity.

Immediately after the stirring period has ended, pour solution into absorbance cell. Measure turbidity for 4 minutes, recording absorbance at 1 minute and maximum reading obtained during the 4-minute period.

C Calibration

Using 100 ml aliquot for each calibration standard prepared in section IX.D, determine a linear regression on 6 points with a correlation coefficient of 0.995.

D. Correction for sample color and turbidity

Run a sample blank using procedures XI.A and XI.B without the addition of barium chloride (XI.A.3).

E. Calculations

Calculate mg/L of SO_4 using linear regression times any dilution factors of a 100 mL sample aliquot.

XII. QUALITY CONTROL

A. Calibration Blank

100 mL of DI water; acceptable limit is <2 mg/L

B. Calibration Standards

2.0 to 40 mg/L; correlation coefficient $\geq$ 0.995

C. ICV Standard

20 mg/L; acceptance limits are ±10% of theoretical value

D. Matrix Spikes and Duplicates

1. For each day or every batch of 10 samples (whichever is most frequent) of similar matrix, one spike sample must be analyzed. Acceptable recovery limit is ±25%.

2. For every day or every batch of 10 samples (whichever is most frequent) of similar matrix, one sample must be prepared and analyzed in duplicate. Acceptable relative percent difference is <20%. If range or RPD exceeds the limits for an aqueous sample matrix, reanalyze the duplicates and 25% of the positive samples in the batch, at a minimum.

E. Continuing Calibration Verification (CCV) Standard: One midrange standard must be analyzed every 10 samples. Acceptance limits are ±10% of Theoretical Value.

F. Continuing Calibration Blank (CCB): One blank must be analyzed every 10 samples. The acceptance limit is <1 mg/L.

XIV. REFERENCES

A. Annual Book of ASTM Standards, Part 31, "Water", Standard D516-68, Method B, p 430 (1976).

B. Standard Methods for the Examination of Water and Wastewater, 8th Edition.

C. EPA Methods for the Chemical Analysis of Water and Wastewater, Method 375.4

D. Sulfate 9038 by Tubridimetric, SW846, 3rd edition.

STANDARD OPERATING PROCEDURE

8270-L
Extractable Base/Neutral and Acid Organic Compounds in Water and Liquid Matrices by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique

SOP NUMBER:	HO-O-008-A
AUTHOR:	Matt Hearne
EFFECTIVE DATE:	July 20, 1993
SUPERSEDES:	None

APPROVAL

Matt Hearne — 7/22/93
Department Supervisor — Date

Simon Lee — 7/22/93
Organic ~~Laboratory~~ Manager — Date

ACCEPTANCE

John Valla — 7-22-93
Quality Assurance Officer — Date

1. PURPOSE

1.1. The purpose of this Standard Operating Procedure (SOP) is to set forth the procedure used for the determination of a number of organic compounds that are partitioned into an organic solvent and are amendable to gas chromatography/mass spectrometry.

2. SCOPE/APPLICATION

2.1. This method is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of liquid waste matrices and waters. Direct injection of a sample may be used in limited applications.

2.2. METHOD BRIEF

2.2.1. A measured amount of sample, approximately 1000 mL, is extracted with methylene chloride using a separatory funnel (9.1.2) or liquid-liquid apparatus (9.1.1). The methylene chloride extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Qualitative identification of the analyte of interest in the extract is performed using the retention time and relative abundance of at least two characteristic masses. Quantitation is performed using the internal standard technique with a single characteristic mass in coordination with the average relative response factor from the initial calibration.

2.3. SAFETY INFORMATION

2.3.1. The toxicity or carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. A current awareness file of OSHA regulations regarding the safe handling of the chemicals specified and a reference file of material safety data sheets is maintained in the laboratory and is available to all personnel involved in the chemical analysis. The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, α-BHC, β-BHC, γ-BHC, dibenzo(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT and

polychlorinated biphenyls (PCBs).

2.4. ANALYTE INFORMATION

2.4.1. This method can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

2.4.2. The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent extraction and exhibits poor chromatographic behavior. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-Nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and can not be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

3. RESPONSIBILITY

3.1. QUALITY ASSURANCE OFFICER

3.1.1. The Quality Assurance Officer has overall responsibility for monitoring implementation of and adherence to the policies and procedures set forth in this document.

3.1.2. The Quality Assurance Officer will conduct semi-annual audits of the

facility to monitor adherence to this and other SOPs. The results of the audit will be reported to Regional Management and Corporate Quality.

3.2. ORGANIC LABORATORY MANAGER/SECTION SUPERVISOR

3.2.1. The manager/supervisor is responsible for ensuring adherence to this SOP.

3.2.2. The manager/supervisor will ensure that this SOP is reviewed on an annual basis.

3.2.3. The manager/supervisor will ensure that the Quality Assurance Office is notified when revisions to the SOP are required.

3.3. ANALYST

3.3.1. The analyst is responsible for following all procedures set forth in this document. The analyst will report any deviations to the procedures set forth in this document.

3.3.2. The analyst is responsible for reviewing the SOP on an annual basis and reporting any required revisions to the department manager or supervisor.

4. REVIEWS/REVISIONS

4.1. This SOP will be reviewed on an annual basis at a minimum.

4.2. At the time of review, any required revisions will be incorporated and the superseded document replaced.

5. DISTRIBUTION

5.1. Distribution of this SOP will be determined by the Quality Assurance Office.

5.2. Distribution records will be maintained by the Quality Assurance Office.

6. GENERAL POLICIES/PROCEDURES

6.1. Initial and continuing calibration standards not specifically meeting the

established method criteria but deemed acceptable will be documented with scientific justification on its corresponding forms. Supervisor approval is required before proceeding with analysis. Non-conformance forms must be completed and routed as appropriate.

6.2. Quality Control results falling outside established acceptance criteria will be documented with scientific justification for acceptance of data or footnoted regarding reanalysis or re-extraction requirements. Supervisor approval is required before proceeding with analysis. Non-conformance forms must be completed and routed as appropriate.

6.3. Surrogate recoveries falling below 10 percent in a sample will require that the sample be re-extracted and re-analyzed. The results must be qualified with appropriate comments regarding the reason for the deficiency (i.e., matrix interferences). Non-conformance forms must be completed and routed as appropriate.

6.4. The tuning standard is not used to assess column performance or injection port inertness as per Method 8270. This criteria is assessed with the data from the continuing calibration.

7. SAMPLE HANDLING AND STORAGE

7.1. CONTAINERS

7.1.1. Containers used to collect samples will be purchased from a source which certifies the cleanliness of its containers, or from a source which has been demonstrated as capable of supplying clean containers through the lab's analysis of bottle blanks or clean samples.

7.2. STORAGE

7.2.1. The samples must be refrigerated at less than 4° C from the time of collection until extraction. The extracts must also be kept refrigerated until analysis.

7.3. HOLDING TIME LIMITS

7.3.1. The samples must be extracted within 7 days from date of collection. The samples must be analyzed within 40 days of sample extraction.

8. APPARATUS AND CHEMICALS

8.1. GLASSWARE/HARDWARE

8.1.1. Drying column - 19 mm ID chromatographic column with coarse frit. (Substitution of a small pad of Pyrex glass wool for the frit will prevent cross contamination of sample extracts.)

8.1.2. Concentrator tube - Kuderna-Danish, 10 mL, graduated. Ground glass stopper is used to prevent evaporation of extracts.

8.1.3. Evaporation flask - Kuderna-Danish, 500 mL. Attach to concentrator tube with springs.

8.1.4. Snyder column - Kuderna-Danish, three ball macro.

8.1.5. Snyder column - Kuderna-Danish, two-ball micro.

8.1.6. Vials - Amber glass, 2 mL capacity with Teflon-lined screw cap.

8.1.7. Silicon carbide boiling chips - approximately 10/40 mesh. Heat to 400° C for 30 minutes or Soxhlet extract with methylene chloride.

8.1.8. Water bath - Heated with concentric ring cover, capable of temperature control (± 2° C). The bath should be used in a hood.

8.1.9. Balance - Analytical, capable of accurately weighing 0.0001 g.

8.1.10. Nitrogen evaporation device equipped with a water bath that can be maintained at 35° C - 40° C.

8.1.11. 2000 mL separatory funnel with teflon stopcock and stopper.

8.1.12. Volumetric flasks - 10-mL, 25-mL, 50-mL, class A with ground-glass

stoppers.

8.1.13. Grab sample bottle 1000 mL, narrow mouth amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

8.1.14. Disposable pasteur glass pipette, 2 mL.

8.1.15. Continuous liquid-liquid extractors - Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor - Ace Glass Company, Vineland, NH, P/N 6841-10 or equivalent).

8.1.16. Gel permeation chromatography (GPC) cleanup device - GPC Autoprep 1002, Analytical Biochemical Labs, Inc., or equivalent.

8.1.17. 25 mm ID x 600-700 mm glass column.

8.1.18. Syringe, 10 mL with Luerlock fitting.

8.1.19. Syringe filter holder and filters - stainless steel and TFE, Gelman 4310 or equivalent.

8.1.20. Glass beads

8.2. REAGENTS AND SARMS

8.2.1. Reagent water - ASTM Type II, organic-free.

8.2.2. Sodium hydroxide solution (10 N) - dissolve 40 g NaOH in reagent water and dilute to 100 mL.

8.2.3. Sodium thiosulfate - (ACS) Granular

8.2.4. Sulfuric acid solution (1:1) - Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

8.2.5. Acetone, methanol, methylene chloride - Pesticide quality or equivalent.

8.2.6. Sodium sulfate - (ACS) Granular, anhydrous. To remove impurities, heat at 400° C for four hours in shallow tray or Soxhlet extract using methylene chloride.

8.2.7. Sodium sulfate - (ACS) Powdered, anhydrous (purified by heating at 400° C for 4 hours in shallow tray).

8.2.8. Target analyte solutions, surrogate solutions, and matrix spike solutions are obtained from various vendors and verified for accuracy. Internal standard solutions are also obtained from vendors in solution form.

8.3. INSTRUMENTATION

8.3.1. Finnigan model 4500 or INCOS-50 gas chromatograph/mass spectrometer, Varian model 3400 gas chromatograph with CTC A200S Autosamplers.

8.3.2. Column - Restek RTX-XTI-5, 30 m x 0.32 mm (ID) bonded-phase silicone coated fused silica capillary column, 1.00 μm film thickness (or equivalent).

8.3.3. Data system - Nova 4X/16 with SuperINCOS version 8.0 or DG-10 with INCOS version 11.0

9. PROCEDURE

9.1. SAMPLE PREPARATION

9.1.1. Continuous Liquid-Liquid Extraction

9.1.1.1 Add methylene chloride to the bottom of the extractor and fill to a depth of 1 inch above the bottom side arm.

9.1.1.2 Using a 1-liter graduated cylinder, measure out a 1-liter sample aliquot and place it into a continuous liquid-

liquid extractor. Pipet 0.5 mL surrogate standard spiking solution into the extractor funnel and mix well. Check the pH of the sample with wide range pH paper and adjust the pH to less than 2.0 with 1:1 sulfuric acid. Add 0.5 mL of BNA matrix spiking solution to each of two 1-liter portions from the sample selected for spking.

9.1.1.3 Add 500 mL of methylene chloride and teflon boiling chips to the distilling flask. Add sufficient reagent water to ensure proper operation. Extract for 18 hours. Record extraction information in the log. Allow to cool, then detach the distilling flask, and label the flask.

9.1.1.4 A method blank is to be prepared with each group of samples extracted. A method blank consists of a 1 liter volume of reagent water, spiked with the surrogate and carried through the entire analytical procedure.

9.1.1.5 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

9.1.1.6 Transfer the extract by pouring the extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate, and collect the extracts in a K-D concentrator flask. Rinse the Erlenmeyer flasks and columns with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

9.1.1.7 Add one or two clean glass beads to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (90 to 100°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation the balls of the column will actively chatter

but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 10 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. If GPC cleanup is required, proceed to Section 9.2. If further sample concentration is necessary, proceed to nitrogen blowdown.

9.1.2 Separatory Funnel Extraction

9.1.2.1 Using a 1-liter graduated cylinder, measure 1 liter of sample and transfer it to the separatory funnel. Add 1.0 mL of the surrogate standards to all samples, spikes, and blanks. For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/uL of each base/neutral analyte and 150 ng/uL of each acid analyte in the extract to be analyzed.

9.1.2.2 Check the pH of the sample with wide-range pH paper and adjust the pH to < 2.

9.1.2.3 Add 60 mL of methylene chloride to the separatory funnel.

9.1.2.4 Seal and shake the separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure. NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once.

9.1.2.5 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass

wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask.

9.1.2.6 Repeat the extraction two more times using fresh portions of solvent (steps 9.1.2.3 through 9.1.2.5). Combine the three solvent extracts.

9.1.2.7 Adjust the pH of the aqueous phase to > 11. Serially extract three times with 60 mL of methylene chloride, as outlined in Paragraphs 9.1.2.3 through 9.1.2.5. Collect and combine the extracts and label the combined extract appropriately.

9.1.2.8 Separate concentration of the acid and base/neutral extracts may be preferable (e.g., if for regulatory purposes the presence or absence of specific acid or base/neutral compounds at low concentrations must be determined, separate extract analyses may be warranted).

9.1.2.9 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

9.1.2.10 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20-30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

9.1.2.11 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the

concentration in 10-20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.2.12 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride. The extract may be further concentrated by using microsnyder or nitrogen blowdown techniques to obtain 1 mL for each fraction.

9.2. EXTRACT CLEAN-UP (OPTIONAL)

9.2.1. GPC set-up and calibration; proceed with GPC clean-up in accordance with PACE, Inc. SOP MN-O-431.

9.3. INITIAL CALIBRATION

9.3.1. The recommended GC/MS operating conditions:

Mass Range:	35-500 amu
Scan Time:	1 sec/scan or less
Initial Temperature:	45° C, hold for 4 minutes
Temperature Program:	45-290° C at 7-10° C/min
Final Temperature:	290° C, hold until benzo (g,h,i) perylene has eluted
Injector Temperature:	250-300° C
Transfer Line Temperature:	250-300° C
Source Temperature:	150 or 300° C
Injector:	Grob-type, splitless
Sample Volume:	1-2 μL
Carrier Gas:	Helium at 12-20 psig

9.3.2. Each GC/MS system must be hardware-tuned to meet the criteria in Table I for a 50 ng injection of decafluorotriphenylphosphine (DFTPP). Analyses should not begin until all these criteria are met. Background subtraction should be straight forward and designed only to eliminate column bleed or instrument background ions. Background

subtraction actions resulting in spectral distortions for the sole purpose of meeting special requirements are contrary to the objectives of Quality Assurance and are unacceptable.

NOTE: Whenever the laboratory takes corrective action which may change the tuning criteria for DFTPP (e.g., ion source cleaning or repair, etc.) the tune must be verified irrespective of the 12-hour tuning requirements.

Definition: The twelve (12) hour time period for GC/MS system tuning and standards calibration (initial or continuing calibration criteria) begins at the moment of injection of the DFTPP analysis that the laboratory submits as documentation of compliant tune. The time period ends after twelve (12) hours has elapsed according to the system clock.

9.3.2.1 The analysis of DFTPP may be performed by:

a) Injection of 50 ng of DFTPP
b) By adding 50 ng to continuing calibration standard

9.3.3. The internal standards given in Table IV should permit most of the components of interest in a chromatogram to have a retention time of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation as given in Table V. If interferences are noted, use the next most intense ion as the quantitation ion (i.e., for 1,4-dichlorobenzene-d_4 use m/z 152 for quantitation).

9.3.4. Prior to the analysis of samples and after tuning criteria have been met, the GC/MS system must be initially calibrated at a minimum of five concentrations to determine the linearity of response utilizing target compound standards.

9.3.5. Analyze 1-2 μL ** of each calibration standard (containing the internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table V).

** If a 1 μL injection is used, the calibration standards should be

made up at 20, 50, 80, 120, 160 µg/mL and fortified with internal standard at 40 µg/mL. If a 2 µL injection is used the calibration standards should be made up at 10, 25, 40, 60, 80 µg/L and fortified with internal standard at 20 µg/mL which would account for 20, 50, 80, 120, 160 ng and 40 ng on column.

Calculate response factors (RFs) for each compound as outlined in Section 10.1, Equation 1.

9.3.6. The average RF should be calculated for each compound. The percent relative standard deviation (Equation 2) should also be calculated for each compound. The %RSD should be less than 30% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) (see Table VII) must be less than 30%. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units.

9.3.7. A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. The System Performance Check Compounds (SPCCs) (See Table VIII) have a minimum acceptable average RF of is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

9.3.8. The initial calibration is valid only after both the %RSD for CCC compounds and the minimum RF for SPCC have been met or justification is given that would support valid generation of data. Only after both these criteria are met can sample analysis begin.

9.4. DAILY GC/MS CALIBRATION

9.4.1. Prior to analysis of samples, the GC/MS tuning standard must be analyzed. A 50-ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table I. These criteria must be demonstrated during each 12 hour shift.

9.4.2. A 50 ng/µL calibration standard containing each compound of interest,

including all required surrogates, must be analyzed every 12 hours during analysis. Compare the response factor data from the standards every 12 hours with the average response factor from the initial calibration for a specific instrument as per the SPCC and CCC criteria.

9.4.3. System Performance Check Compounds (SPCCs): A system performance check must be made during every 12 hour shift. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum RF for semivolatile SPCCs listed in Table VIII is 0.050. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

9.4.4. Calibration Check Compounds (CCC): After the system performance check is met, CCCs listed in Table VII are used to check the validity of the initial calibration. Calculate the percent difference as detailed in Section 10.3.

9.4.5. If the percent difference for any compound is greater than 20%, consider this a warning limit. If the percent difference for each CCC is less than 25%, the continuing calibration is assumed valid. If the criterion is not met for any one CCC, corrective action must be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration must be generated. This criterion must be met before sample analysis begins.

9.4.6. The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last check calibration, the analytical system must be inspected for malfunctions and corrections must be made. If the EICP area for any of the internal standards changes by a factor of two, (-50% to +100%) from the last daily calibration standard check, the MS must be inspected for malfunctions and

corrections must be made.

9.5. GC/MS ANALYSIS

9.5.1. Extracts may be screened on a GC/FID using the same type of capillary column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

9.5.2. The extract obtained from sample preparation should be fortified at 40 μg/mL just prior to analysis such that 40 ng is injected on the column.

9.5.3. Analyze the extract by GC/MS. The volume to be injected should ideally contain 100-ng of base/neutral and 200-ng of acid surrogates for a 1 μL injection.

9.5.4. If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/μL of each internal standard in the extract volume. The diluted extract must be reanalyzed.

9.5.5. Perform all qualitative and quantitative measurements as described in "Data Interpretation". Store the extracts at less than 4°C protected from light in screw-cap or crimp-top vials equipped with unpierced Teflon lined septa.

9.6. DATA INTERPRETATION

9.6.1. Qualitative Analysis - Target Analytes

9.6.1.1. The target compounds shall be identified by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: 1) elution of the sample component at the same GC relative retention time as the standard component, and 2) correspondence of the sample component and standard component mass spectra.

9.6.1.2. For establishing correspondence of the GC relative

retention time (RRT), the sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run during the same 12 hour shift as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest. See Table IV for internal standard assignment.

9.6.1.3. For comparison of standard and sample component mass spectra, mass spectra obtained on each PACE GC/MS system are required.

9.6.1.4. The requirements for qualitative verification by comparison of mass spectra are as follows:

9.6.1.4.1. All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

9.6.1.4.2. The relative intensities of ions specified in 9.6.1.4.1 must agree within plus or minus 20% between the standard and sample spectra.

9.6.1.4.3. Ions greater than 10% in the sample spectrum must be considered and accounted for by the analyst making the comparison.

9.6.2. Guidelines for Making Tentative Identification:

9.6.2.1. A library search may be executed for non-target sample components for the purpose of tentative identification. For this purpose, the EPA/NIH Mass Spectral Library should be used.

9.6.2.2. Up to 20 substances (Contract Specific) of greatest apparent concentration not listed in Table II for the

combined base/neutral/ acid fraction shall be tentatively identified via a forward search of the EPA/NIH mass spectral library. (Substances with responses less than 10% of the nearest internal standard are not required to be searched in this fashion). Only after visual comparison of sample spectra with the nearest library searches will be mass spectral interpretation specialist assign a tentative identification.

9.6.2.3. Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

9.6.2.4. The relative intensities of the major ions should agree within ± 20%.

9.6.2.5. Molecular ions present in reference spectrum should be present in sample spectrum.

9.6.2.6. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

9.6.2.7. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

9.6.2.8. If in the opinion of the mass spectral specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e. unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

9.7. QUANTITATION

9.7.1. Target components identified shall be quantified by the internal

standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte. The EICP area of characteristic ions of analytes listed in Tables V and IX are used. The continuing calibratione response factor (RF) is used to calculate the concentration in the sample. Secondary ions may be used if interferences are present. The area of a secondary ion cannot be substituted for the area of a primary ion unless a response factor is calculated using the secondary ion.

9.7.2. An estimated concentration for non-target components tentatively identified shall be quantified by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

9.7.3. When calculating concentration for non-calibrated components, total area counts from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A response factor of 1.0 is to be assumed. The value from this quantitation shall be qualified as estimated and the nearest resolved internal standard used to quantitate shall be identified. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

9.7.4. Calculate surrogate standard recovery on all samples, blanks and spikes. Determine if recovery is within limits (Table III) and report on appropriate form.

9.7.4.1. If recovery is not within limits, the following is required:

9.7.4.1.1. Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

9.7.4.1.2. Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

9.7.4.1.3. Re-extract and reanalyze the sample if none of the above are a problem.

9.7.4.1.4. Report the data from the first extraction and

document the event. Report the reasons for failure on a non-conformance form.

10. CALCULATIONS

10.1. Calculate response factors (RFs) for each compound as follows:

$$RF = (A_x C_{is})/(A_{is} C_x) \qquad \text{Equation 1}$$

Where:

A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (ng/μL).
C_x = Concentration of the compound being measured (ng/μL).

10.2. The percent relative standard deviation (%RSD) is calculated as follows:

$$\%RSD = 100\,[SD/\overline{RF}] \qquad \text{Equation 2}$$

Where:

$\overline{RF}$ = Mean of the Response Factors mentioned above.
SD = Standard Deviation of initial response.

Where:

$$SD = \sqrt{\sum_{i-1}^{n} \frac{(X_i - \overline{X})^2}{n-1}} \qquad \text{Equation 3}$$

X_i = Each individiual response factor.

$\overline{X}$ = Mean response factor
n = Number of response factors

10.3. The Percent Difference (%D) is calculated as follows:

$$\% \text{ Difference} = \frac{(RF_i - RF_c)\ (100)}{RF_i} \qquad \text{Equation 4}$$

Where:

RF_i = Average response factor from initial calibration
RF_c = Response factor from current verification check standard

10.4. The concentration of analyte in the sample is calculated as follows:

$$\text{Concentration } (\mu g/kg) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(W_o)(V_i)} \quad \text{Equation 5}$$

A_x	=	Area of the characteristic ion for the compound to be measured
A_{is}	=	Area of the characteristic ion for the internal standard
I_s	=	Amount of internal standard injected in nanograms (ng)
W_o	=	Volume of sample extracted in liters
V_i	=	Volume of extract injected (μL)
V_t	=	Volume of total extract
RF_i	=	Average response factor from initial calibration

10.5. Calculate the Matrix Spike Percent Recovery as follows:

$$\text{Matrix Spike Percent Recovery} = \frac{(SSR - SR)}{SA}(100) \quad \text{Equation 6}$$

Where: SSR = Spike Sample Results
SR = Sample Result
SA = Spike Added from spiking mix

10.6. The laboratory will calculate the relative percent difference between the matrix spike and matrix spike duplicate. The relative percent differences (RPD) for each component are calculated using the following equation:

$$RPD = \frac{(2)(A - B)}{(A + B)}(100) \quad \text{Equation 7}$$

Where: RPD = Relative Percent Difference
A = First Sample Value
B = Second Sample Value (duplicate)

11. QUALITY CONTROL

11.1. GENERAL

11.1.1. Each day that analysis is performed, the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., column changed), recalibration of the system must take place.

11.1.2. The performance of the entire analytical system should be checked daily, using data gathered from analyses of blanks, standards, and replicate samples. Significant peak tailing must be corrected.

11.1.3. The precision between replicate analysis of standards and check samples should be evaluated. A properly operating system should perform with an average relative standard deviation of less than 10%.

11.1.4. The GC/MS system must be tuned to meet the DFTPP specifications in Sections 9.3.2 and 9.4.1.

11.1.5. There must be an initial calibration of the system as specified in Section 9.3.

11.1.6. The GC/MS system must meet the CCC and SPCC criteria specified in Section 9.3.6, 9.3.7 and 9.4.3, each 12 hours.

11.2. QC REFERENCE SAMPLE

11.2.1. To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operation.

11.2.1.1. A Quality Control (QC) reference sample concentrate is required containing each analyte at a predetermined concentration in methanol. The QC reference sample concentrate may be prepared from pure standards materials or purchased as certified solutions. If prepared by the laboratory, the QC reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

11.2.1.2. A subset (4 replicates) of the 7 spiked aliquots used to determine method detection limits (MDLs) can be utilized to determine the acceptable accuracy and precision limits.

11.2.1.3. Analyze the QC reference samples according to the method beginning in Section 9.1 with extraction of the samples.

11.2.1.4. Calculate the average recovery (x) in μg/L and the standard deviation of the recovery (s) in μg/L, for each analyte of interest using the four results.

11.2.1.5. For each analyte, compare the s and x with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table XI. If s and x for all analytes meet the acceptable criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual x falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

11.2.1.6. The large number of analytes in Table XI present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

11.2.1.7. When one or more of the analytes tested fail at least one of the acceptance criteria, proceed as follows:

11.2.1.7.1. Locate and correct the source of the problem and repeat the test for all analytes beginning with Section 11.2.1.2.

11.2.1.7.2. Beginning with Section 11.2.1.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the

problem and repeat the test for all compounds of interest beginning with Section 11.2.1.2.

11.3. METHOD BLANK

11.3.1. A method blank is an reagent or deionized water that is carried through the entire analytical scheme (extraction, concentration, and analysis). The volume of water used for the method blank must be approximately equal to the sample aliquots being processed.

11.3.2. Method blank analysis must be performed at the following frequency: once each batch, with every twenty (20) samples of similar concentration and/or sample matrix, or whenever samples are extracted by the same procedure, whichever is more frequent. The method blank associated with a specific set or group of samples must be analyzed on each GC/MS system used to analyze that specific group or set of samples.

11.3.3. A case is a group or a set of samples collected from a particular site over a given period of time.

11.3.4. It is the laboratory's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be minimized.

11.3.5. An acceptable laboratory method blank should meet the criteria of the paragraphs immediately following.

11.3.5.1. A reagent blank for semi-volatile analysis should contain no greater than two times (2x) the quantitation limit of common phthalate esters. The reagent blank must not contain greater than five times (5x) the quantitation limit of any phthalate ester.

11.3.5.2. For all other target compounds not listed above, the reagent blank must contain less than the quantitation limit of any single target analyte. If a laboratory reagent blank exceeds criteria, the laboratory must consider the analytical system out of control. The source of the

contamination investigated and appropriate corrective measures must be taken and documented.

11.3.6. The laboratory will report ALL sample concentration data as UNCORRECTED for blanks.

11.4. LABORATORY CONTROL SAMPLES (LCS)

11.4.1. An LCS and an LCS duplicate shall be analyzed at a frequency of each analytical batch or once per 20 samples, whichever is more frequent. An LCS consists of either a control matrix spiked with analytes representative of the target analytes or a certified reference material.

NOTE: An LCS duplicate is only required if insufficient sample is available to perform the analysis on a matrix as indicated in Section 11.8.

11.4.2. LCS results are used to verify that the precision and bias of the analytical process are within control limits. The results of the LCS are compared to control limits established for both precision and bias to determine usability of the data. At a minimum, the analytes indicated in Table VI are used, however, certain programs may require a more extensive list.

11.5. SURROGATE SPIKE (SS) ANALYSIS

11.5.1. Surrogate standard determinations are performed on all samples and blanks. All samples and blanks are fortified with surrogate spiking compounds before extraction in order to monitor preparation and analysis of samples.

11.5.2. Each sample (including matrix spike and matrix spike duplicate) and blanks are spiked with surrogate compounds prior to extraction. The surrogate spiking compounds shown in Table X are used to fortify each sample or blank with the proper concentrations. Performance based criteria are generated from laboratory results.

11.5.3. Surrogate spike recovery must be evaluated for acceptance by determining whether the concentration (measured as percent recovery) falls inside the recovery limits (Table III) established by the laboratory.

11.6. REAGENT BLANK SURROGATE SPIKE RECOVERY

11.6.1. When the surrogate recovery for any one surrogate compound is outside of the contract required surrogate recovery limits (listed in Table III) for a reagent blank, the laboratory must take the following actions:

11.6.1.1. Check calculations to assure there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc.; also, check instrument performance.

11.6.1.2. Re-analyze the extract if step above fails to reveal the cause of the non-compliant surrogate recoveries.

11.6.1.3. If the measures listed in the preceding three paragraphs fail to correct the problem, the analytical system must be considered out of control. The problem MUST be corrected before continuing.

11.6.1.4. This may mean recalibrating the instrumentation but it may also mean more extensive action. The specific corrective action is left up to the GC/MS supervisor.

11.7. SAMPLE SURROGATE SPIKE RECOVERY

11.7.1. When the surrogate recovery of any one surrogate compound is outside of the contract required recovery limits (listed in Table III) for a sample, it is the responsibility of the laboratory to establish that the deviation is not due to laboratory problems.

11.7.2. The laboratory will document, (in this instance, document means to write down and discuss problem and corrective action(s) taken in the Case Narrative) deviations outside acceptable quality control limits by taking the following actions:

11.7.2.1. Check calculations to assure there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc.; and, check instrument performance.

11.7.2.2. Re-calculate or re-analyze the sample or extract if the step immediately above fails to reveal a problem. If reanalysis of the sample or extract solves the problem, then only the sample data from the analysis with surrogate spike recoveries within the method windows will be submitted.

11.7.2.3. Re-extract and re-analyze the sample if none of the above are a problem.

11.7.2.4. Report the surrogate spike recovery data and the sample data from the original extraction.

11.8. MATRIX SPIKE/MATRIX SPIKE DUPLICATE ANALYSIS (MS/MSD)

11.8.1. In order to evaluate the matrix effects of the sample upon the analytical methodology, the method uses the standard mixes listed in Table VI to be used for matrix spike and matrix spike duplicate analysis.

11.8.2. MS/MSD Frequency of Analysis - A matrix spike and matrix spike duplicate must be performed once each batch or with every twenty (20) samples of similar concentration and/or similar sample matrix, whichever is more frequent. (Note: If sample is not available, an LCS and an LCS duplicate should be analyzed.)

11.8.3. Use the compounds listed in Table VI to prepare matrix spiking solutions. The analytical protocols require that a uniform amount of matrix spiking solution be added to the sample aliquots prior to extraction. Each method allows for optional dilution steps which must be accounted for when calculating percent recovery of the matrix spike and matrix spike duplicate sample.

11.8.4. Samples requiring optional dilutions and chosen as the matrix spike/matrix spike duplicate samples, must be analyzed at the same

dilution as the original unspiked sample.

11.8.5. Individual component recoveries of the matrix spike are calculated using Equation 7.

11.9. SAMPLE ANALYSIS

11.9.1. Samples can be analyzed upon successful completion of the initial QC activities. When twelve (12) hours have elapsed since the initial QC was completed, it is necessary to conduct an instrument tune and calibration check analysis. Any major system maintenance, such as a source cleaning or installation of a new column, may necessitate a retune and recalibration (see Section 9.4). Minor or routine maintenance as defined on each instrument specific run log page should necessitate only the calibration verification.

11.9.2. *Internal Standards Evaluation - Internal standard responses and* retention times in all samples must be evaluated immediately after a run sequence or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds, the analytical system must be inspected for malfunctions and corrections made as required. If the extracted ion current profile (EICP) area for any internal standard changes by more than a factor of two (-50% to 100%), from the latest daily calibration standard, the MS system must be inspected for malfunction and corrections made as appropriate. Breaking off 1 foot of the column or cleaning the injector sleeve often improves high end sensitivity for the late eluting compounds; repositioning or repacking the front end of the column often improves front end column performance. Poor injection technique can also lead to variable IS ratios. After modification, reanalysis of samples analyzed while the system was malfunctioning is necessary.

11.9.3. Each analytical run must also be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound. The initial method calibration requires that the system should not be saturated for high response compounds at 160 ng (for semi-volatile target compounds). If any compound in any sample exceeds the analytical range, that sample must be diluted, the internal standard concentration readjusted, and

the sample reinjected, as described in specific methods.

11.9.4. When using GC/MS computer data processing programs to obtain the sample component spectrum, the processed and the raw spectra must be evaluated. The verification process should favor false positive.

12. REFERENCES

12.1. USEPA SW-846, Method 8270

12.2. PACE, Inc. SOP MN-O-414

12.3. PACE, Inc. SOP MN-O-431

12.4. See Attachments, Appendices, and Tables following

12.5. All references are to the most current revision of the document referenced.

TABLE I

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30.0 - 60.0 percent of mass 198
68	less than 2.0 percent of mass 69
69	Mass 69 relative abundance
70	less than 2.0 percent of mass 69
127	40.0 - 60.0 percent of mass 198
197	less than 1.0 percent of mass 198
198	base peak, 100 percent relative abundance
199	5.0 - 9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	greater than 1.00 percent of mass 198
441	present but less than mass 443
442	greater than 40.0 percent of mass 198
443	17.0 - 23.0 percent of mass 442

TABLE II

ANALYTES AND QUANTITATION LIMITS

Semi-Volatiles	CAS Number	Quantitation Limit, µg/L
Phenol	108-95-2	10
bis(2-Chloroethyl)ether	111-44-4	10
2-Chlorophenol	95-57-8	10
1,3-Dichlorobenzene	541-73-1	10
1,4-Dichlorobenzene	106-46-7	10
Benzyl alcohol	100-51-6	10
1,2-Dichlorobenzene	95-50-1	10
2-Methylphenol	95-48-7	10
bis(2-Chloroisopropyl)ether	108-60-1	10
4-Methylphenol	106-44-5	10
N-Nitroso-di-n-propylamine	621-64-7	10
Hexachloroethane	67-72-1	10
Nitrobenzene	98-95-3	10
Isophorone	78-59-1	10
2-Nitrophenol	88-75-5	10
2,4-Dimethylphenol	105-67-9	10
Benzoic acid	65-85-0	50
bis(2-Chloroethoxy)methane	111-91-1	10
2,4-Dichlorophenol	120-83-2	10
1,2,4-Trichlorobenzene	120-82-1	10

TABLE II (CONTINUED)

ANALYTES AND QUANTITATION LIMITS

Semi-Volatiles	CAS Number	Quantitation Limit, µg/L
Naphthalene	91-20-3	10
4-Chloroaniline	106-47-8	10
Hexachlorobutadiene	87-68-3	10
4-Chloro-3-methylphenol(para-chloro-meta-cresol)	59-50-7	10
2-Methylnaphthalene	91-57-6	10
Hexachlorocyclopentadiene	77-47-4	10
2,4,6-Trichlorophenol	88-06-2	10
2,4,5-Trichlorophenol	95-95-4	50
2-Chloronaphthalene	91-58-7	10
2-Nitroaniline	88-74-4	50
Dimethylphthalate	131-11-3	10
Acenaphthylene	208-96-8	10
3-Nitroaniline	99-09-2	50
Acenaphthene	83-32-9	10
2,4-Dinitrophenol	51-28-5	50
4-Nitrophenol	100-02-7	50
Dibenzofuran	132-64-9	10
2,4-Dinitrotoluene	121-14-2	10
2,6-Dinitrotoluene	606-20-2	10
Diethylphthalate	84-66-2	10

TABLE II (CONTINUED)

ANALYTES AND QUANTITATION LIMITS

Semi-Volatiles	CAS Number	Quantitation Limit, µg/L
4-Chlorophenyl phenyl ether	7005-72-3	10
Fluorene	86-73-7	10
4-Nitroaniline	100-01-6	50
4,6-Dinitro-2-methylphenol	534-52-1	10
N-Nitrosodiphenylamine	86-30-6	10
4-Bromophenyl phenyl ether	101-55-3	10
Hexachlorobenzene	118-74-1	10
Pentachlorophenol	87-86-5	50
Phenanthrene	85-01-8	10
Anthracene	120-12-7	10
Di-n-butylphthalate	84-74-2	10
Fluoranthene	206-44-0	10
Pyrene	129-00-0	10
Butyl benzyl phthalate	85-68-7	10
3,3'-Dichlorobenzidine	91-94-1	20
Benzo(a)anthracene	56-55-3	10
bis(2-Ethylhexyl)phthalate	117-81-7	10
Chrysene	218-01-9	10
Di-n-octylphthalate	117-84-0	10
Benzo(b)fluoranthene	205-99-2	10

TABLE II (CONTINUED)

ANALYTES AND QUANTITATION LIMITS

Semi-Volatiles	CAS Number	Quantitation Limit µg/L
Benzo(k)fluoranthene	207-08-9	10
Benzo(a)pyrene	50-32-8	10
Indeno(1,2,3-cd)pyrene	193-39-5	10
Dibenz(a,h)anthracene	53-70-3	10
Benzo(g,h,i)perylene	191-24-2	10

TABLE III
METHOD REQUIRED SURROGATE SPIKE RECOVERY LIMITS

Fraction	Surrogate Compound	Water
BN	Nitrobenzene-d_5	35-114
BN	2-Fluorobiphenyl	43-116
BN	Terphenyl-d_{14}	33-141
Acid	Phenol-d_6	10-94
Acid	2-Fluorophenol	21-100
Acid	2,4,6-Tribromophenol	10-123
Acid	2-Chlorophenol-d_4	33-110(Advisory)
BN	1,2-Dichlorobenzene-d_4	16-110(Advisory)

TABLE IV

INTERNAL STANDARD METHOD OF QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}	Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
Phenol	Nitrobenzene	Hexachlorocyclo-pentadiene	4,6-Dinitro-2-methylphenol	Pyrene	Di-n-octyl-phthalate
bis(2-Chloroethyl) ether	Isophorone	2,4,6-Trichloro-phenol	N-nitrosodi-phenylamine	Butylbenzyl phthalate	Benzo(b)fluor-anthene
2-Chlorophenol	2-Nitrophenol	2,4,5-Trichloro-phenol	4-Bromophenyl phenyl ether	3,3'-Dichloro-benzidine	Benzo(k)fluor-anthene
1,3-Dichlorobenzene	2,4-Dimethyl-phenol	2-Chloronaphthalene	Hexachloro-benzene	Benzo(a)-anthracene	Benzo(a)pyrene
1,4-Dichlorobenzene	bis(2-Chloro-ethoxy)methane	2-Nitroaniline	Pentachloro-phenol	bis(2-Ethyl-hexyl)phthalate	Indeno(1,2,3-cd)-pyrene
1,2-Dichlorobenzene	2,4-Dichloro-phenol	Dimethylphthalate	Phenanthrene	Chrysene	Dibenz(a,h)-anthracene
2-Methylphenol	1,2,4-Trichloro-benzene	Acenaphthylene	Fluoroanthene	Terphenyl-d_{14} (surr)	Benzo(g,h,i)-perylene
Benzyl alcohol	Naphthalene	3-Nitroaniline	Anthracene		
4-Methylphenol	4-Chloroaniline	Acenaphthene	Di-n-butyl-phthalate		
Phenol-d_5 (surr)	Hexachloro-butadiene	2,4-Dinitrophenol	2,4,6-Tribromo-phenol (surr)		
N-Nitrosi-Di-n-propylamine	4-Chloro-3-methylphenol	4-Nitrophenol			
Hexachloroethane	2-Methyl naphthalene	Dibenzofuran			
2-Fluorophenol (surr)	Nitrobenzene-d_5 (surr)	2,4-Dinitrotoluene			
2-Chlorophenol-d_4 (surr)		2,6-Dinitrotoluene			
1,2-Dichlorobenzene-d_4 (surr)		Diethyl phthalate			
bis(2-chloroisopropyl) ether		4-Chlorophenyl phenyl ether			
		Fluorene			
		4-Nitroaniline			
		2-Fluorobiphenyl (surr)			

surr - surrogate compound

TABLE V

CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET COMPOUNDS

Parameter	Primary Ion	Secondary Ions
Phenol	94	65, 66
bis(2-Chloroethyl) ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 113
1,4-Dichlorobenzene	146	148, 113
Benzyl Alcohol	53	79, 77
1,2-Dichlorobenzene	146	148, 113
2-Methylphenol	53	107
bis-(2-Chloroisopropyl) ether	45	77, 79
4-Methylphenol	53	107
N-Nitroso-Di-n-propylamine	70	42, 101, 130
Hexachloroethane	117	201, 199
Nitrobenzene	77	123, 199
Isophorone	82	95, 138
2-Nitrophenol	139	65, 109
2,4-Dimethylphenol	122	107, 121
Benzoic Acid	122	105, 77
bis(2-Chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145

TABLE V (Continued)

CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET COMPOUNDS

Parameter	Primary Ion	Secondary Ions
Naphthalene	128	129, 127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
2-Chloronaphthalene	162	164, 127
2-Nitroaniline	65	92, 138
Dimethyl Phthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	53 , 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	139	109, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	89	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethylphthalate	149	177, 150

TABLE V (Continued)

CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET COMPOUNDS

Parameter	Primary Ion	Secondary Ions
4-Chlorophenyl Phenyl ether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	92, 53
4,6-Dinitro-2-methylphenol	198	182, 77
N-nitrosodiphenylamine	169	168, 167
4-Bromophenyl Phenyl ether	248	250, 141
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 100
Benzidine	184	92, 185
Pyrene	202	101, 100
Butyl Benzyl Phthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
bis-(2-ethylhexyl)phthalate	149	167, 279
Chrysene	228	226, 229
Di-n-octyl Phthalate	149	-
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 227
Dibenz(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277

TABLE VI

MATRIX SPIKE RECOVERY LIMITS*
(%)

Fraction	Matrix Spike Compound	Recovery	RPD
BN	1,2,4-trichlorobenzene	39-98	28
BN	Acenaphthene	46-118	31
BN	2,4-dinitrotoluene	24-96	38
BN	Pyrene	26-127	31
BN	N-nitroso-di-n-Propylamine	41-116	38
BN	1,4-dichlorobenzene	36-97	28
Acid	Pentachlorophenol	9-103	50
Acid	Phenol	12-89	42
Acid	2-chlorophenol	27-123	40
Acid	4-chloro-3-methylphenol	23-97	42
Acid	4-nitrophenol	10-80	50

* These limits are for advisory purposes only. They are not to be used to determine if a sample should be re-analyzed.

TABLE VII

CALIBRATION CHECK COMPOUNDS (CCC)

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitrosodiphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

TABLE VIII

SYSTEM PERFORMANCE CHECK COMPOUNDS (SPCC)

Base/Neutral Fraction	Acid Fraction
N-nitroso-di-n-propylamine	2,4-dinitrophenol
Hexachlorocyclopentadiene	4-Nitrophenol

TABLE IX

CHARACTERISTIC IONS FOR SEMI-VOLATILE INTERNAL STANDARDS

	Primary Ion	Secondary Ion(s)
1,4-Dichlorobenzene-d_4 (I.S.)	152	150, 115
Naphthalene-d_8 (I.S.)	136	68
Acenaphthene-d_{10} (I.S.)	164	162, 160
Phenanthrene-d_{10} (I.S.)	188	94, 80
Chrysene-d_{12} (I.S.)	240	120, 236
Perylene-d_{12} (I.S)	264	260, 265

TABLE X

SURROGATE SPIKING COMPOUNDS

Compound	Fraction	Water µg/L
Nitrobenzene-d_5	BN	100
2-Fluorobiphenyl	BN	100
Terphenyl-d_{14}	BN	100
Phenol-d_5	Acid	200
2-Fluorophenol	Acid	200
2,4,6-Tribromophenol	Acid	200
2-Chlorophenol-d_4	Acid	200
1,2-Dichlorobenzene-d_4	BN	100

* at the time of injection

TABLE XI

QC ACCEPTANCE CRITERIA

Semi-Volatiles	Test Conc., µg/L	Limit for s, µg/L	Range for x, µg/L, %	Range, p,p$_s$
Phenol	100	22.6	16.6 - 100.0	5 - 112
bis(2-Chloroethyl)ether	100	55.0	42.9 - 126.0	12 - 158
2-Chlorophenol	100	28.7	36.2 - 120.4	23 - 134
1,3-Dichlorobenzene	100	41.7	16.7 - 153.9	D - 172
1,4-Dichlorobenzene	100	32.1	37.3 - 105.7	20 - 124
Benzyl alcohol				
1,2-Dichlorobenzene	100	30.9	48.6 - 112.0	32 - 129
2-Methylphenol				
bis(2-Chloroisopropyl)ether	100	46.3	62.8 - 138.6	36 - 166
4-Methylphenol				
N-Nitroso-di-n-propylamine	100	55.4	13.6 - 197.9	D - 230
Hexachloroethane	100	24.5	55.2 - 100.0	40 - 113
Nitrobenzene	100	39.3	54.3 - 157.6	35 - 180
Isophorone	100	63.3	46.6 - 180.2	21 - 196
2-Nitrophenol	100	35.2	45.0 - 166.7	29 - 182
2,4-Dimethylphenol	100	26.1	41.8 - 109.0	32 - 119
Benzoic acid				
bis(2-Chloroethoxy)methane	100	34.5	49.2 - 164.7	33 - 184
2,4-Dichlorophenol				
1,2,4-Trichlorobenzene	100	28.1	57.3 - 129.2	44 - 142
Naphthalene	100	30.1	35.6 - 119.6	21 - 133
4-Chloroaniline				
Hexachlorobutadiene	100	26.3	37.8 - 102.2	24 - 116
4-Chloro-3-methylphenol	100	37.2	40.8 - 127.9	22 - 147
2-Methylnaphthalene				
Hexachlorocyclopentadiene				
2,4,6-Trichlorophenol	100	31.7	52.4 - 129.2	37 - 144
2,4,5-Trichlorophenol				
2-Chloronaphthalene	100	13.0	34.5 - 113.5	60 - 118

TABLE XI, CONTINUED

QC ACCEPTANCE CRITERIA

Semi-Volatiles	Test Conc., µg/L	Limit for s, µg/L	Range for x, µg/L, %	Range, p, p_s
2-Nitroaniline				
Dimethylphthalate	100	23.2	D - 100.0	D - 112
Acenaphthylene	100	40.2	53.5 - 126.0	33 - 145
3-Nitroaniline				
Acenaphthene	100	27.6	60.1 - 132.3	47 - 145
2,4-Dinitrophenol	100	49.8	D - 172.9	D - 191
4-Nitrophenol	100	47.2	13.0 - 106.5	D - 132
Dibenzofuran				
2,4-Dinitrotoluene	100	21.8	47.5 - 126.9	39 - 139
2,6-Dinitrotoluene	100	29.6	68.1 - 136.7	50 - 158
Diethylphthalate	100	26.5	D - 100.0	D - 114
4-Chlorophenyl phenyl ether	100	33.4	38.4 - 144.7	25 - 158
Fluorene	100	20.7	71.6 - 108.4	59 - 121
4-Nitroaniline				
4,6-Dinitro-2-methylphenol	100	93.2	53.0 - 100.0	D - 181
N-Nitrosodiphenylamine				
4-Bromophenyl phenyl ether	100	23.0	64.9 - 114.4	53 - 127
Hexachlorobenzene	100	24.9	7.8 - 141.5	D - 152
Pentachlorophenol	100	48.9	38.1 - 151.8	14 - 176
Phenanthrene	100	20.6	65.2 - 108.7	54 - 120
Anthracene	100	32.0	43.4 - 118.0	27 - 133
Di-n-butylphthalate	100	16.7	8.4 - 111.0	1 - 118
Fluoranthene	100	32.8	42.9 - 121.3	26 - 137
Pyrene	100	25.2	69.6 - 100.0	52 - 115
Butyl benzyl phthalate	100	23.4	D - 139.9	D - 152

TABLE XI, CONTINUED

QC ACCEPTANCE CRITERIA

Semi-Volatiles	Test Conc., µg/L	Limit for s, µg/L	Range for x, µg/L, %	Range, p,p_s
3,3'-Dichlorobenzidine	100	71.4	8.2 - 212.5	D - 262
Benzo(a)anthracene	100	27.6	41.8 - 133.3	33 - 143
bis(2-Ethylhexyl)phthalate	100	41.1	28.9 - 136.8	8 - 158
Chrysene	100	48.3	44.1 - 139.9	17 - 168
Di-n-octylphthalate	100	31.4	18.6 - 131.8	4 - 146
Benzo(b)fluoranthene	100	38.8	42.0 - 140.4	24 - 159
Benzo(k)fluoranthene	100	32.3	25.2 - 145.7	11 - 162
Benzo(a)pyrene	100	39.0	31.7 - 148.0	17 - 163
Indeno(1,2,3-cd)pyrene	100	44.6	D - 150.9	D - 171
Dibenzo(a,h)anthracene	100	70.0	D - 199.7	D - 227
Benzo(g,h,i)perylene	100	58.9	D - 195.0	D - 219

STANDARD OPERATING PROCEDURE

8270-S
Extractable Base/Neutral and Acid Organic Compounds in Soil and Solid Waste Matrices by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique

SOP NUMBER:	HO-O-009-A
AUTHOR:	Matt Hearne
EFFECTIVE DATE:	July 20, 1993
SUPERSEDES:	None

APPROVAL

Matt Hearne — Department Supervisor — 7/22/93 — Date

Simon Li — Organic Laboratory Manager — 7/22/93 — Date

ACCEPTANCE

Quality Assurance Officer — 7-22-93 — Date

1. PURPOSE

1.1. The purpose of this Standard Operating Procedure (SOP) is to set forth the procedure used for the determination of a number of organic compounds that are partitioned into an organic solvent and are amendable to gas chromatography/mass spectrometry.

2. SCOPE/APPLICATION

2.1. This method is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices and soils. Direct injection of a sample may be used in limited applications.

2.2. METHOD BRIEF

2.2.1. A measured amount of sample, approximately 30 grams, is extracted with 1:1 methylene chloride-acetone using sonication techniques. The methylene chloride-acetone extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Qualitative identification of the analyte of interest in the extract is performed using the retention time and relative abundance of at least two characteristic masses. Quantitation is performed using the internal standard technique with a single characteristic mass in coordination with the average relative response factor from the initial calibration.

2.3. SAFETY INFORMATION

2.3.1. The toxicity or carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. A current awareness file of OSHA regulations regarding the safe handling of the chemicals specified and a reference file of material safety data sheets is maintained in the laboratory and is available to all personnel involved in the chemical analysis. The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, α-BHC, β-BHC, γ-BHC, dibenzo(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT and polychlorinated biphenyls (PCBs).

2.4. ANALYTE INFORMATION

2.4.1. This method can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

2.4.2. The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent extraction and exhibits poor chromatographic behavior. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-Nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and can not be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

3. RESPONSIBILITY

3.1. QUALITY ASSURANCE OFFICER

3.1.1. The Quality Assurance Officer has overall responsibility for monitoring implementation of and adherence to the policies and procedures set forth in this document.

3.1.2. The Quality Assurance Officer will conduct semi-annual audits of the facility to monitor adherence to this and other SOPs. The results of the audit will be reported to Regional Management and Corporate Quality.

3.2. ORGANIC LABORATORY MANAGER/SECTION SUPERVISOR

3.2.1. The manager/supervisor is responsible for ensuring adherence to this SOP.

3.2.2. The manager/supervisor will ensure that this SOP is reviewed on an annual basis.

3.2.3. The manager/supervisor will ensure that the Quality Assurance Office is notified when revisions to the SOP are required.

3.3. ANALYST

3.3.1. The analyst is responsible for following all procedures set forth in this document. The analyst will report any deviations to the procedures set forth in this document.

3.3.2. The analyst is responsible for reviewing the SOP on an annual basis and reporting any required revisions to the department manager or supervisor.

4. REVIEWS/REVISIONS

4.1. This SOP will be reviewed on an annual basis at a minimum.

4.2. At the time of review, any required revisions will be incorporated and the superseded document replaced.

5. DISTRIBUTION

5.1. Distribution of this SOP will be determined by the Quality Assurance Office.

5.2. Distribution records will be maintained by the Quality Assurance Office.

6. GENERAL POLICIES/PROCEDURES

6.1 Initial and continuing calibration standards not specifically meeting the established method criteria but deemed acceptable will be documented with scientific justification on its corresponding forms. Supervisor approval is required before proceeding with analysis. Non-conformance forms must be completed and routed as appropriate.

6.2. Quality Control results falling outside established acceptance criteria will be documented with scientific justification for acceptance of data or footnoted regarding reanalysis or re-extraction requirements. Supervisor approval is required before proceeding with analysis. Non-conformance forms must be completed and routed as appropriate.

6.3. Surrogate recoveries falling below 10 percent in a sample will require that the sample be re-extracted and re-analyzed. The results must be qualified with appropriate comments regarding the reason for the deficiency (i.e., matrix interferences). Non-conformance forms must be completed and routed as appropriate.

6.4. The tuning standard is not used to assess column performance or injection port inertness as per Method 8270. This criteria is assessed with the data from the continuing calibration.

7. SAMPLE HANDLING AND STORAGE

7.1. CONTAINERS

7.1.1. Containers used to collect samples will be purchased from a source which certifies the cleanliness of its containers, or from a source which has been demonstrated as capable of supplying clean containers through the lab's analysis of bottle blanks or clean samples.

7.2. STORAGE

7.2.1. The samples must be refrigerated at less than 4°C from the time of collection until extraction. The extracts must also be kept refrigerated until analysis.

7.3. HOLDING TIME LIMITS

7.3.1. The samples must be extracted within 14 days from date of collection. The samples must be analyzed within 40 days of sample extraction.

8. APPARATUS AND CHEMICALS

8.1. GLASSWARE/HARDWARE

8.1.1. Drying column - 19 mm ID chromatographic column with coarse frit. (Substitution of a small pad of Pyrex glass wool for the frit will prevent cross contamination of sample extracts.)

8.1.2. Concentrator tube - Kuderna-Danish, 10 mL, graduated. Ground glass stopper is used to prevent evaporation of extracts.

8.1.3. Evaporation flask - Kuderna-Danish, 500 mL. Attach to concentrator tube with springs.

8.1.4. Snyder column - Kuderna-Danish, three ball macro.

8.1.5. Snyder column - Kuderna-Danish, two-ball micro.

8.1.6. Vials - Amber glass, 2 mL capacity with Teflon-lined screw cap.

8.1.7. Silicon carbide boiling chips - approximately 10/40 mesh. Heat to 400° C for 30 minutes or Soxhlet extract with methylene chloride.

8.1.8. Water bath - Heated with concentric ring cover, capable of temperature control (± 2° C). The bath should be used in a hood.

8.1.9. Balance - Analytical, capable of accurately weighing 0.0001 g.

8.1.10. Nitrogen evaporation device equipped with a water bath that can be maintained at 35° C - 40° C.

8.1.11. Gel permeation chromatography (GPC) cleanup device: see SOP MN-O-431.

8.1.12. Volumetric flasks - 10-mL, 25-mL, 50-mL, class A with ground-glass stoppers.

8.1.13. Grab sample bottle 250 mL, wide mouth amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

8.1.14. Apparatus for determining percent moisture:

8.1.14.0.1. Oven, drying

8.1.14.0.2. Desiccator

8.1.14.0.3. Crucibles, porcelain or aluminum weighing boats.

8.1.14.0.4. Disposable Pasteur glass pipets - 1 mL.

8.1.15. Sonication equipment: see PACE, Inc. SOP MN-O-414

8.1.16. Side arm flask - 500 mL

8.1.17. Hirsch funnel

8.1.18. Ashless filter paper

8.1.19. Flat bottom boiling flask - 500 mL

8.1.20. 2 mL autosampler vials

8.2. REAGENTS AND SARMS

8.2.1. Reagent water - ASTM Type II, organic-free

8.2.2. Sodium hydroxide solution (10 N) - dissolve 40 g NaOH in reagent water and dilute to 100 mL.

8.2.3. Sodium thiosulfate - (ACS) Granular

8.2.4. Sulfuric acid solution (1:1) Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

8.2.5. Acetone, methanol, methylene chloride - Pesticide quality or equivalent.

8.2.6. Sodium sulfate - (ACS) Granular, anhydrous. To remove impurities, heat at 400° C for four hours in shallow tray or Soxhlet extract using methylene chloride.

8.2.7. Sodium sulfate - (ACS) Powdered, anhydrous (purified by heating at 400° C for four hours in shallow tray).

8.2.8. Target analyte solutions, surrogate solutions, and matrix spike solutions are obtained from various vendors and verified for accuracy. Internal standard solutions are also obtained from vendors in solution form.

8.3. INSTRUMENTATION

8.3.1. Finnegan model 4500 or INCOS 50 gas chromatograph/mass spectrometer with Varian model 3400 gas chromatograph and CTC A200S autosampler.

8.3.2. Column - Restek XTI-5, 30 m x 0.32 mm (ID) bonded-phase silicon coated fused silica capillary column, 1.00 µm film thickness (or equivalent).

8.3.3. Data system - Nova 4X/16 with SuperINCOS version 8.0 or DG-10 with INCOS 50 version 11.0.

9. PROCEDURE

9.1. SAMPLE PREPARATION

9.1.1. Proceed with sample preparation as described in SOP MN-O-414.

9.2. EXTRACT CLEAN-UP (OPTIONAL)

9.2.1. GPC set-up and calibration; proceed with GPC clean-up in accordance with PACE, Inc. SOP MN-O-431.

9.3. INITIAL CALIBRATION

9.3.1. The recommended GC/MS operating conditions:

Mass Range:	35-500 amu
Scan Time:	1 sec/scan or less
Initial Temperature:	40° C, hold for 4 minutes
Temperature Program:	40-290° C at 7-10° C/min
Final Temperature:	290° C, hold until benzo (g,h,i) perylene has eluted
Injector Temperature:	250-300° C
Transfer Line Temperature:	250-300° C
Source Temperature:	150 or 300° C
Injector:	Grob-type, splitless
Sample Volume:	1-2 μL
Carrier Gas:	Helium at 12-20 psig

If regionally specific operating conditions are used, they may be found in Appendix A-1.

9.3.2. Each GC/MS system must be hardware-tuned to meet the criteria in Table I for a 50 ng injection of decafluorotriphenylphosphine (DFTPP). Analyses should not begin until all these criteria are met. Background subtraction should be straight forward and designed only to eliminate column bleed or instrument background ions. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting special requirements are contrary to the objectives of Quality Assurance and are unacceptable.

NOTE: Whenever the laboratory takes corrective action which may change the tuning criteria for DFTPP (e.g., ion source cleaning or repair, etc.) the tune must be verified irrespective of the 12-hour tuning requirements.

Definition: The twelve (12) hour time period for GC/MS system tuning and standards calibration (initial or continuing calibration criteria) begins at the moment of injection of the DFTPP analysis that the laboratory submits as documentation of compliant tune. The time period ends after twelve (12) hours has elapsed according to the system clock.

9.3.2.1 The analysis of DFTPP may be performed by:

a) Injection of 50 ng of DFTPP
b) By adding 50 ng to continuing calibration standard

9.3.3. The internal standards given in Table IV should permit most of the components of interest in a chromatogram to have a retention time of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation as given in Table V. If interferences are noted, use the next most intense ion as the quantitation ion (i.e., for 1,4-dichlorobenzene-d_4 use m/z 152 for quantitation).

9.3.4. Prior to the analysis of samples and after tuning criteria have been met, the GC/MS system must be initially calibrated at a minimum of five concentrations to determine the linearity of response utilizing target compound standards.

9.3.5. Analyze 1-2 μL ** of each calibration standard (containing the internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table V).

** If a 1 μL injection is used, the calibration standards should be made up at 20, 50, 80, 120, 160 μg/mL and fortified with internal standard at 40 μg/mL. If a 2 μL injection is used the calibration standards should be made up at 10, 25, 40, 60, 80 μg/L and fortified with internal standard at 20 μg/mL which

would account for 20, 50, 80, 120, 160 ng and 40 ng on column.

Calculate response factors (RFs) for each compound as outlined in Section 10.1, Equation 1.

9.3.6. The average RF should be calculated for each compound. The percent relative standard deviation (Equation 2) should also be calculated for each compound. The %RSD should be less than 30% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) (see Table VII) must be less than 30%. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units.

9.3.7. A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. The System Performance Check Compounds (SPCCs) (See Table VIII) have a minimum acceptable average RF of 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

9.3.8. The initial calibration is valid only after both the %RSD for CCC compounds and the minimum RF for SPCC have been met or justification is given that would support valid generation of data. Only after both these criteria are met can sample analysis begin.

9.4. DAILY GC/MS CALIBRATION

9.4.1. Prior to analysis of samples, the GC/MS tuning standard must be analyzed. A 50-ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table I. These criteria must be demonstrated during each 12 hour shift.

9.4.2. A 50 ng/μL calibration standard containing each compound of interest, including all required surrogates, must be analyzed every 12 hours during analysis. Compare the response factor data from the standards every 12 hours with the average response factor from the initial calibration for a specific instrument as per the SPCC and CCC criteria.

9.4.3. System Performance Check Compounds (SPCCs): A system performance check must be made during every 12 hour shift. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum RF for semivolatile SPCCs listed in Table VIII is 0.050. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

9.4.4. Calibration Check Compounds (CCC): After the system performance check is met, CCCs listed in Table VII are used to check the validity of the initial calibration. Calculate the percent difference as detailed in Section 10.3.

9.4.5. If the percent difference for any compound is greater than 20%, consider this a warning limit. If the percent difference for each CCC is less than 25%, the continuing calibration is assumed valid. If the criterion is not met for any one CCC, corrective action must be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration must be generated. This criterion must be met before sample analysis begins.

9.4.6. The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last check calibration, the analytical system must be inspected for malfunctions and corrections must be made. If the EICP area for any of the internal standards changes by a factor of two, (-50% to +100%) from the last daily calibration standard check, the MS must be inspected for malfunctions and corrections must be made.

9.5. GC/MS ANALYSIS

9.5.1. It is highly recommended that the extract be screened on a GC/FID

using the same type of capillary column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

9.5.2. The extract obtained from sample preparation should be fortified at 40 µg/mL just prior to analysis such that 40 ng is injected on the column.

9.5.3. Analyze the extract by GC/MS. The volume to be injected should ideally contain 100-ng of base/neutral and 200-ng of acid surrogates for a 1 µL injection.

9.5.4. If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/µL of each internal standard in the extract volume. The diluted extract must be reanalyzed.

9.5.5. Perform all qualitative and quantitative measurements as described in "Data Interpretation". Store the extracts at less than 4°C protected from light in screw-cap or crimp-top vials equipped with unpierced Teflon lined septa.

9.6. DATA INTERPRETATION

9.6.1. Qualitative Analysis - Target Analytes

9.6.1.1. The target compounds shall be identified by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: 1) elution of the sample component at the same GC relative retention time as the standard component, and 2) correspondence of the sample component and standard component mass spectra.

9.6.1.2. For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run during the same 12 hour shift as the sample. If

coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest. See Table IV for internal standard assignment.

9.6.1.3. For comparison of standard and sample component mass spectra, mass spectra obtained on each PACE GC/MS system are required.

9.6.1.4. The requirements for qualitative verification by comparison of mass spectra are as follows:

9.6.1.4.1. All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

9.6.1.4.2. The relative intensities of ions specified in 9.6.1.4.1 must agree within plus or minus 20% between the standard and sample spectra.

9.6.1.4.3. Ions greater than 10% in the sample spectrum must be considered and accounted for by the analyst making the comparison.

9.6.2. Guidelines for Making Tentative Identification:

9.6.2.1. A library search may be executed for non-target sample components for the purpose of tentative identification. For this purpose, the EPA/NIH Mass Spectral Library should be used.

9.6.2.2. Up to 20 substances (Contract Specific) of greatest apparent concentration not listed in Table II for the combined base/neutral/ acid fraction shall be tentatively identified via a forward search of the EPA/NIH mass spectral library. (Substances with responses less than 10% of the nearest internal standard are not required to

be searched in this fashion). Only after visual comparison of sample spectra with the nearest library searches will be mass spectral interpretation specialist assign a tentative identification.

9.6.2.3. Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

9.6.2.4. The relative intensities of the major ions should agree within ± 20%.

9.6.2.5. Molecular ions present in reference spectrum should be present in sample spectrum.

9.6.2.6. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

9.6.2.7. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

9.6.2.8. If in the opinion of the mass spectral specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e. unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

9.7. QUANTITATION

9.7.1. Target components identified shall be quantified by the internal standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte. The EICP area of characteristic ions of analytes listed in Tables V and IX are used. The continuing calibration response factor (RF) is used to calculate the

concentration in the sample. Secondary ions may be used if interferences are present. The area of a secondary ion cannot be substituted for the area of a primary ion unless a response factor is calculated using the secondary ion.

9.7.2. An estimated concentration for non-target components tentatively identified shall be quantified by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

9.7.3. When calculating concentration for non-calibrated components, total area counts from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A response factor of 1.0 is to be assumed. The value from this quantitation shall be qualified as estimated and the internal standard used to quantitate shall be identified. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

9.7.4. Calculate surrogate standard recovery on all samples, blanks and spikes. Determine if recovery is within limits and report on appropriate form.

9.7.4.1. If recovery is not within limits, the following is required:

9.7.4.1.1. Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

9.7.4.1.2. Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

9.7.4.1.3. Re-extract and reanalyze the sample if none of the above are a problem.

9.7.4.1.4. Report the data from first extractions and document the event. Report the reasons for failure on a non-conformance form.

10. CALCULATIONS

10.1. Calculate response factors (RFs) for each compound as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$ Equation 1

Where:

A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (ng/μL).
C_x = Concentration of the compound being measured (ng/μL).

10.2. The percent relative standard deviation (%RSD) is calculated as follows:

$$\%RSD = 100\ [SD/\overline{RF}]$$ Equation 2

Where:

$\overline{RF}$ = Mean of the Response Factors mentioned above.
SD = Standard Deviation of initial response.

Where:

$$SD = \sqrt{\sum_{i-1}^{n} \frac{(X_i - \overline{X})^2}{n-1}}$$ Equation 3

X_i = Each individiual response factor.

$\overline{X}$ = Mean response factor
n = Number of response factors

10.3. The Percent Difference (%D) is calculated as follows:

$$\%\ Difference = \frac{(RF_i - RF_c)\ (100)}{RF_i}$$ Equation 4

Where:

RF_i = Average response factor from initial calibration
RF_c = Response factor from current verification check standard

10.4. The concentration of analyte in the sample is calculated as follows:

$$\text{Concentration } (\mu g/kg) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(W_o)(V_i)(D)} \quad \text{Equation 5}$$

A_x = Area of the characteristic ion for the compound to be measured
A_{is} = Area of the characteristic ion for the internal standard
I_s = Amount of internal standard injected in nanograms (ng)
W_o = Weight of sample extracted in grams
V_i = Volume of extract injected (μL)
V_t = Volume of total extract
RF_i = Average response factor from initial calibration

$$D = \frac{100 \text{ \% moisture}}{100} \quad \text{Equation 6}$$

10.5. Calculate the Matrix Spike Percent Recovery as follows:

$$\text{Matrix Spike Percent Recovery} = \frac{(SSR - SR)}{SA}(100) \quad \text{Equation 7}$$

Where: SSR = Spike Sample Results
SR = Sample Result
SA = Spike Added from spiking mix

10.6. The laboratory will calculate the relative percent difference between the matrix spike and matrix spike duplicate. The relative percent differences (RPD) for each component are calculated using the following equation:

$$RPD = \frac{(2)(A - B)}{(A + B)}(100) \quad \text{Equation 8}$$

Where: RPD = Relative Percent Difference
A = First Sample Value
B = Second Sample Value (duplicate)

11. QUALITY CONTROL

11.1. GENERAL

11.1.1. Each day that analysis is performed, the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., column changed), recalibration of the system must take place.

11.1.2. The performance of the entire analytical system should be checked daily, using data gathered from analyses of blanks, standards, and replicate samples. Significant peak tailing must be corrected.

11.1.3. The precision between replicate analysis of standards and check samples should be evaluated. A properly operating system should perform with an average relative standard deviation of less than 10%.

11.1.4. The GC/MS system must be tuned to meet the DFTPP specifications in Sections 9.3.2 and 9.4.1.

11.1.5. There must be an initial calibration of the system as specified in Section 9.3.

11.1.6. The GC/MS system must meet the SPCC criteria specified in Section 9.3.7 and 9.4.3, each 12 hours.

11.2. QC REFERENCE SAMPLE

11.2.1. To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operation.

11.2.1.1. A Quality Control (QC) reference sample concentrate is required containing each analyte at a predetermined concentration in methanol. The QC reference sample concentrate may be prepared from pure standards materials or purchased as certified solutions. If prepared by the laboratory, the QC reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

11.2.1.2. A subset (4 replicates) of the 7 spiked aliquots used to determine method detection limits (MDLs) can be utilized to determine the acceptable accuracy and precision limits.

11.2.1.3. Analyze the QC reference samples according to the method beginning in Section 9.1 with extraction of the samples.

11.2.1.4. Calculate the average recovery (x) in μg/L and the standard deviation of the recovery (s) in μg/L, for each analyte of interest using the four results.

11.2.1.5. For each analyte, compare the s and x with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table XI. If s and x for all analytes meet the acceptable criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual x falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

11.2.1.6. The large number of analytes in Table XI present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

11.2.1.7. When one or more of the analytes tested fail at least one of the acceptance criteria, proceed as follows:

11.2.1.7.1. Locate and correct the source of the problem and repeat the test for all analytes beginning with Section 11.2.1.2.

11.2.1.7.2. Beginning with Section 11.2.1.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 11.2.1.2.

11.3. METHOD BLANK

11.3.1. A method blank is an aliquot of organic-free soil or sodium sulfate that is carried through the entire analytical scheme (extraction, concentration, and analysis). The quantity of the soil used for the method blank must be approximately equal to the sample aliquots being processed.

11.3.2. Method blank analysis must be performed at the following frequency: once each batch, with every twenty (20) samples of similar concentration and/or sample matrix or whenever samples are extracted by the same procedure, whichever is more frequent. The method blank associated with a specific set or group of samples must be analyzed on each GC/MS system used to analyze that specific group or set of samples.

11.3.3. A case is a group or a set of samples collected from a particular site over a given period of time.

11.3.4. It is the laboratory's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be minimized.

11.3.5. An acceptable laboratory method blank should meet the criteria of the paragraphs immediately following.

11.3.5.1. A reagent blank for semi-volatile analysis should contain

no greater than two times (2x) the quantitation limit of common phthalate esters. The reagent blank must not contain greater than five times (5x) the quantitation limit of any phthalate ester.

11.3.5.2. For all other target compounds not listed above, the reagent blank must contain less than the quantitation limit of any single target analyte. If a laboratory reagent blank exceeds criteria, the laboratory must consider the analytical system out of control. The source of the contamination investigated and appropriate corrective measures must be taken and documented.

11.3.6. The laboratory will report ALL sample concentration data as UNCORRECTED for blanks.

11.4. LABORATORY CONTROL SAMPLES (LCS)

11.4.1. An LCS and an LCS duplicate shall be analyzed at a frequency of each analytical batch or once per 20 samples, whichever is more frequent. An LCS consists of either a control matrix spiked with analytes representative of the target analytes or a certified reference material.

NOTE: An LCS duplicate is only required if insufficient sample is available to perform the analysis on a matrix as indicated in Section 11.8.

11.4.2. LCS results are used to verify that the precision and bias of the analytical process are within control limits. The results of the LCS are compared to control limits established for both precision and bias to determine usability of the data. At a minimum, the analytes indicated in Table VI are used, however, certain programs may require a more extensive list.

11.5. SURROGATE SPIKE (SS) ANALYSIS

11.5.1. Surrogate standard determinations are performed on all samples and blanks. All samples and blanks are fortified with surrogate spiking compounds before extraction in order to monitor preparation and analysis of samples.

11.5.2. Each sample (including matrix spike and matrix spike duplicate) and blanks are spiked with surrogate compounds prior to extraction. The *surrogate spiking compounds shown in* Table X are used to fortify each sample or blank with the proper concentrations. Performance based criteria are generated from laboratory results.

11.5.3. Surrogate spike recovery must be evaluated for acceptance by determining whether the concentration (measured as percent recovery) falls inside the recovery limits established by the laboratory.

11.6. REAGENT BLANK SURROGATE SPIKE RECOVERY

11.6.1. When the surrogate recovery for any one surrogate compound is outside of the contract required surrogate recovery limits (listed in Table III) for a reagent blank, the laboratory must take the following actions:

11.6.1.1. Check calculations to assure there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc.; also, check instrument performance.

11.6.1.2. Re-analyze the extract if step above fails to reveal the cause of the non-compliant surrogate recoveries.

11.6.1.3. If the measures listed in the preceding three paragraphs fail to correct the problem, the analytical system must be considered out of control. The problem MUST be corrected before continuing.

11.6.1.4. This may mean recalibrating the instrumentation but it may also mean more extensive action. The specific corrective action is left up to the GC/MS supervisor.

11.7. SAMPLE SURROGATE SPIKE RECOVERY

11.7.1. When the surrogate recovery of any one surrogate compound is outside of the contract required recovery limits (listed in Table III) for a sample, it is the responsibility of the laboratory to establish that the deviation is not due to laboratory problems.

11.7.2. The laboratory will document, (in this instance, document means to write down and discuss problem and corrective action(s) taken in the Case Narrative) deviations outside acceptable quality control limits by taking the following actions:

11.7.2.1. Check calculations to assure there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc.; and, check instrument performance.

11.7.2.2. Re-calculate or re-analyze the sample or extract if the step immediately above fails to reveal a problem. If reanalysis of the sample or extract solves the problem, then only the sample data from the analysis with surrogate spike recoveries within the method windows will be submitted.

11.7.2.3. Re-extract and re-analyze the sample if none of the above are a problem.

11.7.2.4. Report the surrogate spike recovery data and the sample data from the original extraction.

11.8. MATRIX SPIKE/MATRIX SPIKE DUPLICATE ANALYSIS (MS/MSD)

11.8.1. In order to evaluate the matrix effects of the sample upon the analytical methodology, the method uses the standard mixes listed in Table VI to be used for matrix spike and matrix spike duplicate analysis.

11.8.2. MS/MSD Frequency of Analysis - A matrix spike and matrix spike duplicate must be performed once each batch or with every twenty (20) samples of similar concentration and/or similar sample matrix, whichever is more frequent. (Note: If sample is not available, an LCS and an LCS duplicate should be analyzed.)

11.8.3. Use the compounds listed in Table VI to prepare matrix spiking solutions. The analytical protocols require that a uniform amount of matrix spiking solution be added to the sample aliquots prior to extraction. Each method allows for optional dilution steps which must

be accounted for when calculating percent recovery of the matrix spike and matrix spike duplicate sample.

11.8.4. Samples requiring optional dilutions and chosen as the matrix spike/matrix spike duplicate samples, must be analyzed at the same dilution as the original unspiked sample.

11.8.5. Individual component recoveries of the matrix spike are calculated using Equation 7.

11.9. SAMPLE ANALYSIS

11.9.1. Samples can be analyzed upon successful completion of the initial QC activities. When twelve (12) hours have elapsed since the initial QC was completed, it is necessary to conduct an instrument tune and calibration check analysis. Any major system maintenance, such as a source cleaning or installation of a new column, may necessitate a retune and recalibration (see Section 9.4). Minor or routine maintenance as defined on each instrument specific run log page should necessitate only the calibration verification.

11.9.2. Internal Standards Evaluation - Internal standard responses and retention times in all samples must be evaluated immediately after a run sequence or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds, the analytical system must be inspected for malfunctions and corrections made as required. If the extracted ion current profile (EICP) area for any internal standard changes by more than a factor of two (-50% to 100%), from the latest daily calibration standard, the MS system must be inspected for malfunction and corrections made as appropriate. Breaking off 1 foot of the column or cleaning the injector sleeve often improves high end sensitivity for the late eluting compounds; repositioning or repacking the front end of the column often improves front end column performance. Poor injection technique can also lead to variable IS ratios. After modification, reanalysis of samples analyzed while the system was malfunctioning is necessary.

11.9.3. Each analytical run must also be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral

characteristics of that compound. The initial method calibration requires that the system should not be saturated for high response compounds at 160 ng (for semi-volatile target compounds). If any compound in any sample exceeds the analytical range, that sample must be diluted, the internal standard concentration readjusted, and the sample reinjected, as described in specific methods.

11.9.4. When using GC/MS computer data processing programs to obtain the sample component spectrum, the processed and the raw spectra must be evaluated. The verification process should favor false positive.

12. REFERENCES

12.1. USEPA SW-846, Method 8270

12.2. PACE, Inc. SOP MN-O-414

12.3. PACE, Inc. SOP MN-O-431

12.4. See Attachments, Appendices, and Tables following

12.5. All references are to the most current revision of the document referenced.

TABLE I

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30.0 - 60.0 percent of mass 198
68	less than 2.0 percent of mass 69
69	Mass 69 relative abundance
70	less than 2.0 percent of mass 69
127	40.0 - 60.0 percent of mass 198
197	less than 1.0 percent of mass 198
198	base peak, 100 percent relative abundance
199	5.0 - 9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	greater than 1.00 percent of mass 198
441	present but less than mass 443
442	greater than 40.0 percent of mass 198
443	17.0 - 23.0 percent of mass 442

TABLE II

ANALYTES AND QUANTITATION LIMITS

Semi-Volatiles	CAS Number	Quantitation Limit, µg/kg
Phenol	108-95-2	330
bis(2-Chloroethyl)ether	111-44-4	330
2-Chlorophenol	95-57-8	330
1,3-Dichlorobenzene	541-73-1	330
1,4-Dichlorobenzene	106-46-7	330
Benzyl alcohol	100-51-6	330
1,2-Dichlorobenzene	95-50-1	330
2-Methylphenol	95-48-7	330
bis(2-Chloroisopropyl)ether	108-60-1	330
4-Methylphenol	106-44-5	330
N-Nitroso-di-n-propylamine	621-64-7	330
Hexachloroethane	67-72-1	330
Nitrobenzene	98-95-3	330
Isophorone	78-59-1	330
2-Nitrophenol	88-75-5	330
2,4-Dimethylphenol	105-67-9	330
Benzoic acid	65-85-0	1600
bis(2-Chloroethoxy)methane	111-91-1	330
2,4-Dichlorophenol	120-83-2	330
1,2,4-Trichlorobenzene	120-82-1	330

TABLE II (CONTINUED)

ANALYTES AND QUANTITATION LIMITS

Semi-Volatiles	CAS Number	Quantitation Limit, µg/kg
Naphthalene	91-20-3	330
4-Chloroaniline	106-47-8	330
Hexachlorobutadiene	87-68-3	330
4-Chloro-3-methylphenol(para-chloro-meta-cresol)	59-50-7	330
2-Methylnaphthalene	91-57-6	330
Hexachlorocyclopentadiene	77-47-4	330
2,4,6-Trichlorophenol	88-06-2	330
2,4,5-Trichlorophenol	95-95-4	1600
2-Chloronaphthalene	91-58-7	330
2-Nitroaniline	88-74-4	1600
Dimethylphthalate	131-11-3	330
Acenaphthylene	208-96-8	330
3-Nitroaniline	99-09-2	1600
Acenaphthene	83-32-9	330
2,4-Dinitrophenol	51-28-5	1600
4-Nitrophenol	100-02-7	1600
Dibenzofuran	132-64-9	330
2,4-Dinitrotoluene	121-14-2	330
2,6-Dinitrotoluene	606-20-2	330
Diethylphthalate	84-66-2	330

TABLE II (CONTINUED)

ANALYTES AND QUANTITATION LIMITS

Semi-Volatiles	CAS Number	Quantitation Limit, µg/kg
4-Chlorophenyl phenyl ether	7005-72-3	330
Fluorene	86-73-7	330
4-Nitroaniline	100-01-6	1600
4,6-Dinitro-2-methylphenol	534-52-1	1600
N-Nitrosodiphenylamine	86-30-6	330
4-Bromophenyl phenyl ether	101-55-3	330
Hexachlorobenzene	118-74-1	330
Pentachlorophenol	87-86-5	1600
Phenanthrene	85-01-8	330
Anthracene	120-12-7	330
Di-n-butylphthalate	84-74-2	330
Fluoranthene	206-44-0	330
Pyrene	129-00-0	330
Butyl benzyl phthalate	85-68-7	330
3,3'-Dichlorobenzidine	91-94-1	660
Benzo(a)anthracene	56-55-3	330
bis(2-Ethylhexyl)phthalate	117-81-7	330
Chrysene	218-01-9	330
Di-n-octylphthalate	117-84-0	330
Benzo(b)fluoranthene	205-99-2	330

TABLE II (CONTINUED)

ANALYTES AND QUANTITATION LIMITS

Semi-Volatiles	CAS Number	Quantitation Limit, µg/kg
Benzo(k)fluoranthene	207-08-9	330
Benzo(a)pyrene	50-32-8	330
Indeno(1,2,3-cd)pyrene	193-39-5	330
Dibenz(a,h)anthracene	53-70-3	330
Benzo(g,h,i)perylene	191-24-2	330

TABLE III
METHOD REQUIRED SURROGATE SPIKE RECOVERY LIMITS

Fraction	Surrogate Compound	Low/Medium Soil
BN	Nitrobenzene-d_5	23-120
BN	2-Fluorobiphenyl	30-115
BN	Terphenyl-d_{14}	18-137
Acid	Phenol-d_6	24-113
Acid	2-Fluorophenol	25-121
Acid	2,4,6-Tribromophenol	19-122
Acid	2-Chlorophenol-d_4	20-130(Advisory)
BN	1,2-Dichlorobenzene-d_4	20-130(Advisory)

TABLE IV

INTERNAL STANDARD METHOD OF QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}	Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
Phenol	Nitrobenzene	Hexachlorocyclo-pentadiene	4,6-Dinitro-2-methylphenol	Pyrene	Di-n-octyl-phthalate
bis(2-Chloroethyl) ether	Isophorone	2,4,6-Trichloro-phenol	N-nitrosodi-phenylamine	Butylbenzyl phthalate	Benzo(b)fluor-anthene
2-Chlorophenol	2-Nitrophenol	2,4,5-Trichloro-phenol	4-Bromophenyl phenyl ether	3,3'-Dichloro-benzidine	Benzo(k)fluor-anthene
1,3-Dichlorobenzene	2,4-Dimethyl-phenol	2-Chloronaphthalene	Hexachloro-benzene	Benzo(a)-anthracene	Benzo(a)pyrene
1,4-Dichlorobenzene	bis(2-Chloro-ethoxy)methane	2-Nitroaniline	Pentachloro-phenol	bis(2-Ethyl-hexyl)phthalate	Indeno(1,2,3-cd)-pyrene
1,2-Dichlorobenzene	2,4-Dichloro-phenol	Dimethylphthalate	Phenanthrene	Chrysene	Dibenz(a,h)-anthracene
2-Methylphenol	1,2,4-Trichloro-benzene	Acenaphthylene	Fluoroanthene	Terphenyl-d_{14} (surr)	Benzo(g,h,i)-perylene
Benzyl alcohol	Naphthalene	3-Nitroaniline	Anthracene		
4-Methylphenol	4-Chloroaniline	Acenaphthene	Di-n-butyl-phthalate		
Phenol-d_5 (surr)	Hexachloro-butadiene	2,4-Dinitrophenol	2,4,6-Tribromo-phenol (surr)		
N-Nitrosi-Di-n-propylamine	4-Chloro-3-methylphenol	4-Nitrophenol			
Hexachloroethane	2-Methyl naphthalene	Dibenzofuran			
2-Fluorophenol (surr)	Nitrobenzene-d_5 (surr)	2,4-Dinitrotoluene			
2-Chlorophenol-d_4 (surr)		2,6-Dinitrotoluene			
1,2-Dichlorobenzene-d_4 (surr)		Diethyl phthalate			
bis(2-chloroisopropyl) ether		4-Chlorophenyl phenyl ether			
		Fluorene			
		4-Nitroaniline			
		2-Fluorobiphenyl (surr)			

surr - surrogate compound

TABLE V

CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET COMPOUNDS

Parameter	Primary Ion	Secondary Ions
Phenol	94	65, 66
bis(2-Chloroethyl) ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 113
1,4-Dichlorobenzene	146	148, 113
Benzyl Alcohol	53	79, 77
1,2-Dichlorobenzene	146	148, 113
2-Methylphenol	53	107
bis-(2-Chloroisopropyl) ether	45	77, 79
4-Methylphenol	53	107
N-Nitroso-Di-n-propylamine	70	42, 101, 130
Hexachloroethane	117	201, 199
Nitrobenzene	77	123, 199
Isophorone	82	95, 138
2-Nitrophenol	139	65, 109
2,4-Dimethylphenol	122	107, 121
Benzoic Acid	122	105, 77
bis(2-Chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145

TABLE V (Continued)

CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET COMPOUNDS

Parameter	Primary Ion	Secondary Ions
Naphthalene	128	129, 127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
2-Chloronaphthalene	162	164, 127
2-Nitroaniline	65	92, 138
Dimethyl Phthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	53 , 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	139	109, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	89	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethylphthalate	149	177, 150

TABLE V (Continued)

CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET COMPOUNDS

Parameter	Primary Ion	Secondary Ions
4-Chlorophenyl Phenyl ether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	92, 53
4,6-Dinitro-2-methylphenol	198	182, 77
N-nitrosodiphenylamine	169	168, 167
4-Bromophenyl Phenyl ether	248	250, 141
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 100
Benzidine	184	92, 185
Pyrene	202	101, 100
Butyl Benzyl Phthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
bis-(2-ethylhexyl)phthalate	149	167, 279
Chrysene	228	226, 229
Di-n-octyl Phthalate	149	-
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 227
Dibenz(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277

TABLE VI

MATRIX SPIKE RECOVERY LIMITS*
(%)

Fraction	Matrix Spike Compound	Recovery	RPD
BN	1,2,4-trichlorobenzene	38-107	23
BN	Acenaphthene	31-137	19
BN	2,4-dinitrotoluene	28-89	47
BN	Pyrene	35-142	36
BN	N-nitroso-di-n-Propylamine	41-126	38
BN	1,4-dichlorobenzene	28-104	27
Acid	Pentachlorophenol	17-109	47
Acid	Phenol	26-90	35
Acid	2-chlorophenol	25-102	50
Acid	4-chloro-3-methylphenol	26-103	33
Acid	4-nitrophenol	11-114	50

* These limits are for advisory purposes only. They are not to be used to determine if a sample should be re-analyzed.

TABLE VII

CALIBRATION CHECK COMPOUNDS (CCC)

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitrosodiphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

TABLE VIII

SYSTEM PERFORMANCE CHECK COMPOUNDS (SPCC)

Base/Neutral Fraction	Acid Fraction
N-nitroso-di-n-propylamine	2,4-dinitrophenol
Hexachlorocyclopentadiene	4-Nitrophenol

TABLE IX

CHARACTERISTIC IONS FOR SEMI-VOLATILE INTERNAL STANDARDS

	Primary Ion	Secondary Ion(s)
1,4-Dichlorobenzene-d_4 (I.S.)	152	150, 115
Naphthalene-d_8 (I.S.)	136	68
Acenaphthene-d_{10} (I.S.)	164	162, 160
Phenanthrene-d_{10} (I.S.)	188	94, 80
Chrysene-d_{12} (I.S.)	240	120, 236
Perylene-d_{12} (I.S)	264	260, 265

TABLE X

SURROGATE SPIKING COMPOUNDS

Compound	Fraction	Low Soil, µg/kg
Nitrobenzene-d_5	BN	100
2-Fluorobiphenyl	BN	100
Terphenyl-d_{14}	BN	100
Phenol-d_5	Acid	200
2-Fluorophenol	Acid	200
2,4,6-Tribromophenol	Acid	200
2-Chlorophenol-d_4	Acid	200
1,2-Dichlorobenzene-d_4	BN	100

* at the time of injection

TABLE XI

QC ACCEPTANCE CRITERIA

Semi-Volatiles	Test Conc., µg/L	Limit for s, µg/L	Range for x, µg/L, %	Range, p, p_s
Phenol	100	22.6	16.6 - 100.0	5 - 112
bis(2-Chloroethyl)ether	100	55.0	42.9 - 126.0	12 - 158
2-Chlorophenol	100	28.7	36.2 - 120.4	23 - 134
1,3-Dichlorobenzene	100	41.7	16.7 - 153.9	D - 172
1,4-Dichlorobenzene	100	32.1	37.3 - 105.7	20 - 124
Benzyl alcohol				
1,2-Dichlorobenzene	100	30.9	48.6 - 112.0	32 - 129
2-Methylphenol				
bis(2-Chloroisopropyl)ether	100	46.3	62.8 - 138.6	36 - 166
4-Methylphenol				
N-Nitroso-di-n-propylamine	100	55.4	13.6 - 197.9	D - 230
Hexachloroethane	100	24.5	55.2 - 100.0	40 - 113
Nitrobenzene	100	39.3	54.3 - 157.6	35 - 180
Isophorone	100	63.3	46.6 - 180.2	21 - 196
2-Nitrophenol	100	35.2	45.0 - 166.7	29 - 182
2,4-Dimethylphenol	100	26.1	41.8 - 109.0	32 - 119
Benzoic acid				
bis(2-Chloroethoxy)methane	100	34.5	49.2 - 164.7	33 - 184
2,4-Dichlorophenol				
1,2,4-Trichlorobenzene	100	28.1	57.3 - 129.2	44 - 142
Naphthalene	100	30.1	35.6 - 119.6	21 - 133
4-Chloroaniline				
Hexachlorobutadiene	100	26.3	37.8 - 102.2	24 - 116
4-Chloro-3-methylphenol	100	37.2	40.8 - 127.9	22 - 147
2-Methylnaphthalene				
Hexachlorocyclopentadiene				
2,4,6-Trichlorophenol	100	31.7	52.4 - 129.2	37 - 144
2,4,5-Trichlorophenol				
2-Chloronaphthalene	100	13.0	34.5 - 113.5	60 - 118

TABLE XI, CONTINUED

QC ACCEPTANCE CRITERIA

Semi-Volatiles	Test Conc., µg/L	Limit for s, µg/L	Range for x, µg/L, %	Range, p,p_s
2-Nitroaniline				
Dimethylphthalate	100	23.2	D - 100.0	D - 112
Acenaphthylene	100	40.2	53.5 - 126.0	33 - 145
3-Nitroaniline				
Acenaphthene	100	27.6	60.1 - 132.3	47 - 145
2,4-Dinitrophenol	100	49.8	D - 172.9	D - 191
4-Nitrophenol	100	47.2	13.0 - 106.5	D - 132
Dibenzofuran				
2,4-Dinitrotoluene	100	21.8	47.5 - 126.9	39 - 139
2,6-Dinitrotoluene	100	29.6	68.1 - 136.7	50 - 158
Diethylphthalate	100	26.5	D - 100.0	D - 114
4-Chlorophenyl phenyl ether	100	33.4	38.4 - 144.7	25 - 158
Fluorene	100	20.7	71.6 - 108.4	59 - 121
4-Nitroaniline				
4,6-Dinitro-2-methylphenol	100	93.2	53.0 - 100.0	D - 181
N-Nitrosodiphenylamine				
4-Bromophenyl phenyl ether	100	23.0	64.9 - 114.4	53 - 127
Hexachlorobenzene	100	24.9	7.8 - 141.5	D - 152
Pentachlorophenol	100	48.9	38.1 - 151.8	14 - 176
Phenanthrene	100	20.6	65.2 - 108.7	54 - 120
Anthracene	100	32.0	43.4 - 118.0	27 - 133
Di-n-butylphthalate	100	16.7	8.4 - 111.0	1 - 118
Fluoranthene	100	32.8	42.9 - 121.3	26 - 137
Pyrene	100	25.2	69.6 - 100.0	52 - 115
Butyl benzyl phthalate	100	23.4	D - 139.9	D - 152

TABLE XI, CONTINUED

QC ACCEPTANCE CRITERIA

Semi-Volatiles	Test Conc., µg/L	Limit for s, µg/L	Range for x, µg/L, %	Range, p, p_s
3,3'-Dichlorobenzidine	100	71.4	8.2 - 212.5	D - 262
Benzo(a)anthracene	100	27.6	41.8 - 133.3	33 - 143
bis(2-Ethylhexyl)phthalate	100	41.1	28.9 - 136.8	8 - 158
Chrysene	100	48.3	44.1 - 139.9	17 - 168
Di-n-octylphthalate	100	31.4	18.6 - 131.8	4 - 146
Benzo(b)fluoranthene	100	38.8	42.0 - 140.4	24 - 159
Benzo(k)fluoranthene	100	32.3	25.2 - 145.7	11 - 162
Benzo(a)pyrene	100	39.0	31.7 - 148.0	17 - 163
Indeno(1,2,3-cd)pyrene	100	44.6	D - 150.9	D - 171
Dibenzo(a,h)anthracene	100	70.0	D - 199.7	D - 227
Benzo(g,h,i)perylene	100	58.9	D - 195.0	D - 219

STANDARD OPERATING PROCEDURE

Ammonia Distillation
Automated Alpkem Method

SOP Number	HO-I-008-B
Author	Bruce Brown
Effective Date	January 14, 1997
Supersedes	HO-I-008-A

Approvals:

Bruce Brown 1/23/97

General Chemistry Supervisor Date

1/23/97

Quality Assurance Officer Date

I. SCOPE AND APPLICATION

A. This distillation method covers the determination of ammonia-nitrogen, exclusive of total Kjeldahl nitrogen, in drinking, surface and saline waters, domestic and industrial wastes.

B. This method covers the range from about 0.05 to 10.0 mg/L NH_3 as N when color developed on the Alpkem.

C. This method is described for macro glassware; however, micro distillation equipment may also be used.

II. SUMMARY OF METHODS

A. The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, as is then distilled into a solution of sulfuric acid. The ammonia in the distillate can be determined colorimetrically with the Alpkem autoanalyzer.

B. In this method, ammonia reacts with alkaline hypochlorite and phenol to form indophenol blue. Sodium nitroferricyanide accelerates the formation of indophenol blue which is measured at 640 nm.

III. INTERFERENCES

A. Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out. Volatile alkaline compounds such as certain ketones, aldehydes and alcohols may cause an off-color upon nesslerization in the distillation method. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH (approximately 2 to 3) prior to distillation.

B. The sample should be checked for residual chlorine at the time of arrival and dechlorinated before analysis.

C. During color development, precipitation of calcium and magnesium hydroxides is eliminated by the addition of a combined potassium sodium tartrate/sodium citrate complexing reagent. Turbid samples must be filtered or centrifuged prior to determination. Samples with background absorbance at the analytical wavelength may interfere.

IV. SAMPLE HANDLING AND PRESERVATION

A. Determine unpreserved samples immediately upon collection. Samples may be preserved with 2 mL of concentrated sulfuric acid per liter of sample and refrigerated at 4^0C. The holding time for preserved samples is 28 days.

V. SAFETY INFORMATION

A. Each chemical compound used in this SOP should be treated as a potential health hazard. Care should be used while handling samples because of toxicity. Exposure to these substances must be reduced to the lowest possible level by whatever means available (i.e., gloves, lab coats, eye protection, fume goods). Reference files of OSHA regulations and Material Safety Data Sheets (MSDSs) are available to all personnel involved in this analysis.

VI. RESPONSIBILITIES

A. Analysts

1. All analysts performing this procedure are responsible for strict adherence to the SOP.

2. Analysts are responsible for ensuring that any deviations to this SOP are reported.

3. Analysts are responsible for reporting to the section supervisor any required revisions to the SOP.

B. Department Supervisors/Managers

1. The department supervisor/manager is responsible for ensuring adherence to this SOP.

2. The department supervisor/manager is responsible for performing an annual review of this SOP and reporting any required revisions to the Quality Assurance Officer.

C. Quality Assurance Officer (QAO)

1. The QAO is responsible for conducting semi-annual laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Regional Management and Corporate Quality.

2. The QAO is responsible for ensuring that all revisions to the SOP are implemented.

3. The QAO is responsible for determining distribution of and maintenance of document control for this SOP.

VII. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. Required revisions will be incorporated at the time of the review.

C. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

VIII. DISTRIBUTION

Distribution of this SOP will be determined by the Quality Assurance Officer.

IX. APPARATUS

A. An all glass distilling apparatus (see diagram)

B. Alpkem autoanalyzer with ammonia/TKN analytical cartridge

C. 100 mL beakers

D. 50 mL graduated cylinder.

X. REAGENTS

A. Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

Note: All solutions must be made with ammonia-free water.

B. 100 mg/L as N ammonium chloride stock standard: Dissolve 0.3819g NH_4Cl in distilled water and bring to volume in a 1 liter volumetric flask.

C. 100 mg/L as N ammonium chloride ICV standard: Dissolved 0.3819g NH_4Cl (from a separate source than the ammonium chloride stock standard) in distilled water and bring to volume in a liter volumetric flask.

D. Borate buffer: Add 88 mL of 0.1 N NaOH solution to 500 mL of 0.025 M sodium tetraborate solution (5.0 g anhydrous $Na_2B_4O_7$ or 9.5 g $Na_2B_4O_7 \cdot 10H_2O$ per liter) and dilute to 1 liter.

E. 1.08 N Sulfuric acid: Slowly add 60 mL of concentrated H_2SO_4 into 100 mL DI water in a 2000 mL volumetric flask and bring to the mark with DI water.

F. Phenolphthalein Solution: commercially available

G. 6.667 mg/L - LCS standard: Add 2.0 mL of the 100 mg/L ammonium chloride stock standard to 30 mL of DI and distill along with every 20 samples.

XI. ALPKEM REAGENTS

For best results, filter all reagents prior to use

A. All reagents and calibrants are prepared with ammonia free deionized of distilled water. See operation note for preparation of ammonia-free deionized water.

1. Stock Complexing Reagent (1 L)

   a. Potassium Sodium Tartrate - 33 g $KNaC_4H_4O_7 \cdot 4H_2O$ (FW 282.23)

   b. Sodium Citrate - 24 g $Na_3C_6H_5O_7 \cdot 2H_2O$

   c. Deionized Water

   d. Sulfuric Acid - H_2SO_4

   Dissolve 33 g of potassium sodium tartrate and 24 g of sodium citrate in approximately 800 mL of deionized water contained in a 1 L beaker. Please the beaker on top of a magnetic stirrer. Insert a magnetic stirring bar and a pH electrode into the solution. Adjust the pH of the solution to pH 5.0 with the sulfuric acid. Transfer the complexing reagent to a 1 L volumetric flask and dilute to the mark with deionized water.

2. Working Complexing Reagent (100 mL)

   a. Stock Complexing Reagent - 100 mL

   b. Brij-35 ®, 30% w/v - 0.5 mL (10 drops)

Add 10 drops of Brij-35 ® for each 100 mL of complexing reagent required for the day's run.

3. Stock 10N Sodium Hydroxide (1 L)

   a. Sodium Hydroxide - 400 g NaOH (FW 40.00)

   b. Deionized Water

   Cautiously add 400 g of sodium hydroxide to approximately 700 ml of deionized water contained in a 1 L volumetric flask. Cool the solution when adding the sodium hydroxide. When the solution is cool, dilute it to the mark with deionized water.

   Caution: This dissolution of sodium hydroxide in water releases a great amount of heat.

4. Alkaline Phenol (1 L)

   a. 10N Sodium Hydroxide - 90 mL

   b. Phenol, liquefied - 94 mL Phenol C_6H_5OH (FW 94.11) liquefied at 88%

   c. Deionized water

Place a 1L volumetric flask that contains approximately 700 mL of deionized water and a magnetic stirring bar into an ice bath positioned on top of a magnetic stirrer. While stirring, add 90 mL of 10N sodium hydroxide. When the solution is cold, slowly add 94 mL of liquefied phenol in small quantities, cooling after each addition. Dilute the solution to the mark with deionized water and mix it well. The resulting solution should be a light straw color. Store the reagent in a brown bottle and refrigerate it at 2-6^{0}C. Stability is approximately 1 month. Discard the reagent if it becomes dark amber in color.

5. Sodium Hypochlorite (100 mL)

   a. Sodium Hypochlorite solution - 20 mL NaOCl, 5.25% solution, household bleach

   b. Deionized Water

   Add 20 mL of sodium hypochlorite solution to approximately 75 mL of deionized water contained in a 100 mL volumetric flask. Dilute the solution to

the mark with deionized water. Mix well and transfer to an amber bottle. This reagent is not stable and should be prepared daily.

6. Sodium Nitroferricyanide (1 L)

   a. Sodium Nitroferricyanide - 0.5 g $Na_2Fe(CN)_5NO \cdot 2H_2O$ (FW 297.97)

   b. Deionized water

   Add 0.5 g of sodium nitroferricyanide to approximately 800 mL of deionized water contained in a 1 L volumetric flask. Dilute the solution to the mark with deionized water. Store this solution in an amber bottle at room temperature where it is stable for at least one month.

7. Diluent (100 mL): Add 10 drops of Brij-35 ® to 100 mL of DI to match sample and calibrant matrices.

8. Sampler Wash Solution: Add 50 mL of 1.08 N H_2SO_4 to 250 mL of DI to match sample and calibrant matrices.

XII. PROCEDURE

A. Fill distillation apparatus with DI water then turn on condenser, water supply and heating mantel. After water in apparatus begins to boil, steam clean with DI water.

B. Pour 30 mL of sample, measured in a graduated cylinder, into a clean Kjeldahl flask and add several drops of phenolphthalein solution. Attach flask to stream apparatus and secure with rubber bands. Add sufficient 10N NaOH through the reagent addition funnel to turn the sample in the flask deep pink.

C. Add 10 ml of borate buffer through the reagent additions funnell and distill 25 mL at the rate 6-10 ml/min into 5.0 mL of 1.08 N H_2SO_4 contained in a 100 mL beaker.

D. **Note**: The condenser tip or an extension of the condenser tip must extend below the level of the sulfuric acid solution.

   Bring 25 mL of distillate up to a final volume of 30 mL with DI water in a graduated cylinder. If samples are not to be color developed at this time, store in a parafilm covered beaker and refrigerate until the next day's analysis.

XIII. ALPKEM COLOR DEVELOPMENT

A. Prep Procedure

1. Set the spectrophotometer and the sampler to the following parameters:

a. Photometer parameters:

Filter	640nm
Flow cell:	Stainless, 10 mm
Absorbance Range:	1 AUFS
Damping (RC):	1s
Bubble Gate:	ON

b. Sample parameters:

Analysis Rate:	120/hr
Sample Time:	20s
Wash Time:	10s
Pecking:	ON
Probe:	Stainless Steel

c. Manifold start-up solution

Deionized water with Brij-35 ® (1 mL L^{-1})

d. Cleaning solution

KimWash (Alpkem P/N A01-5555-26) or 1N NaOH

B. Set up pump tubing and analytical cartridge to the following diagram then follow the general Alpkem operating procedure that follows:

C. Prepare calibration standards

All standards are preserved with 16.67 mL of 1.08 N H_2SO_4

Calibration blank: 16.67 mL of 1.08 N H_2SO_4 to 100 mL final volume
Standard 1: (0.1 mg/L)0.1 mL of 100 ppm NH_3 standard to 100 mL final volume
Standard 2: (0.5mg/L)0.5 mL of 100 ppm NH_3 standard to 100 mL final volume
Standard 3: (1.0 mg/L)1.0 mL of 100 ppm NH_3 standard to 100 mL final volume
Standard 4: (2.5 mg/L)2.5 mL of 100 ppm NH_3 standard to 100 mL final volume
Standard 5: (5.0 mg/L)5.0 mL of 100 ppm NH_3 standard to 100 mL final volume
Standard 6:(10.0 mg/L)10.0 mL of 100 ppm NH_3 standard to 100 mL final volume

ICV: (5.0 mg/L)5.0 mL of 100 ppm NH_3 standard to 100 mL final volume

D. Create sample identification file

1. *Turn on the computer disk drive, screen and printer*
2. After warm up and 640 KB display (C:\>), type "Alpkem" [ENTER]
3. Strike [ENTER] key when ready
4. Enter appropriate ACF file ([ENTER] to bypass 2nd channel)
5. Under primary commands, select A: Create File
6. Under **A: Create File**, select **1: Sample Identification File**
7. Enter filename: Month, Day, Year and Number of days run (ex. 02119101 -- February 11, 1991, 1st run of the day)
8. Enter comment: Name of parameter to be run and any applicable explanations
9. Apply constant dilution factors? Yes
10. Prompt for dilute factors? No [ENTER]
11. Apply constant sample weights? [ENTER]
12. Prompt for sample weights? [ENTER]
13. Enter constant dilution factor: Usually 1.0
14. Do you wish sequential sample ID number? [ENTER]
15. Enter sample ID for CUP #2: Standard 6 (Highest range standard)
16. Enter rest of run using 2 of each calibration standards listed in ACF (Separate each set by blanks). Then enter the samples with their QA, and CCVs and CCBs.

E. Clean the platens and the pump rollers with isopropyl alcohol.

1. Check the platens for excessive wear and replace them if necessary.

2. The pump roller carriage may be turned by hand for access to all of the rollers to clean them after clearing the previous test tubing.

F. Install the appropriate board and reagent lines

1. Retrieve the board from the drawer and carefully unwrap the reagent lines.

2. Connect the heat bath electric line to the correct plug and set the board into the module; bringing the reagent lines to drape in front of the module.

3. Inspect the reagent lines and connections for wear, splits, cracks, and solid clogs, and replace if necessary.

4. Inspect the hoses for wear at the point of the pump roller crossing and replace them if misshapen and flattened.

5. Inspect the mixing coils, manifolds, and connectors for cracks, leaks or clogs, and replace or clean them as necessary.

6. Inspect and install, as needed according to the Alpkem diagrams, all the air lines, sampler wash feed lines, waste lines and debubbler waste lines.

7. Connect the sample line to the sample probe.

8. Position the reagent, sample, waste, sample wash, debubbler waste and air lines in an arrangement across the pump rollers so that

   a. both sides of each platen will have at least one line under it (use dummy lines if needed)

   b. the lines closest in size share a platen

   c. the lines have no sharp bends or kinks

   d. the lines all neatly go to their destinations with a minimum of confusion and tension.

9. Install the platens (if the unit is on, leave one unclamped to keep the pump from starting) using the least worn for the reagent and the sample lines, and the more worn for air, waste and sample wash lines.

10. Place the reagent lines into DI water and/or the appropriate start-up solution bottles.

G. Install the appropriate filters and the flow cell to the spec.

1. Select the appropriate filters from the jar according to the Alpkem diagram.

2. Wipe the filters with Kim Wipes and gently remove any particles of dust with air.

3. Screw the filters into the special housing (glass side in) until they are snug.

4. Select the appropriate flow cell according to the Alpkem diagram and inspect it for cleanliness (gently back flush if necessary using syringe). Make sure the flow cell is completely dry after flushing it by wiping with a KimWipe.

5. Install the flow cell drain tube to the side of the flow cell closest to the spec and connect the other side of the flowcell to the flow cell feed line from the last mixing coil.

6. Gently install the flow cell to the sample side of the spec positioned between the filter and the light source. Tighten this snugly with an allen wrench. Install the reference cell to the reference filter and the light source; tighten this snugly with an allen wrench.

7. Place the flow cell drain tube and any other waste lines in the waste hole on the board.

H. Run the system on the appropriate start up solutions.

1. Verify that the front module switches are on for the sampler, light source, pump module and the heat bath.

2. Clamp all of the platens down and turn on the system with the switch located on the master power supply box. The pump should immediately start. If not,

   a. Check that the platens are securely clamped

   b. All the appropriate switches are on

   c. All the plugs into the master power supply box are securely tied in

   d. Turn off the system and check the fuse located in the main power plug to the master power supply box.

3. Verify that the light source is illuminated, if not:

a. Check the light source "on" switch

b. Check the light source plug to the power box.

c. Check the light source bulb by unscrewing the light source cable from the back of the module and replace it if blown.

4. Verify that the spectrophotometer is functioning by seeing a voltage display. If not,

a. Check all on/off switches.

b. Check all of the plugs.

c. Verify the light source.

d. Check the mast fuse.

5. Make the initial calibration settings

a. Put the bubble gate switch on the side of the spectrophotometer in the "on" position if not using a debubbler on the flow cell, and "off" if one is used.

b. Set the damping control on top of the spec to position indicated by Alpkem spectrophotometer parameters.

c. Set the calibration control on the top of spec to 60.

d. Allow the system to run until all the air is out of all lines and coils with evenly spaced bubbles going through the flow cell. Also, allow the heat bath to come to the correct temperature at this time.

I. Adjust the bubble phasing to achieve an acceptable pattern (if a debubbler is not used on the flow cell)

1. The bubble phase control is a selector switch located in the back of the pump modules (reference manual). Turning the switch allows preset adjustment of the phasing between the pumps downstroke and the valves injection of the bubble into the manifold. The optimum theoretical setting is a bubble injection simultaneous with the pumps downstroke, but often something slightly different is what is required. Strokes are denoted with a click sound. Adjust the control so that the bubbles injected are:

a. Single - split bubbles are out of phase with stroke

b. Correct size and equal in size

c. Oval (not round) and regularly spaced

d. There are not intermediate bubbles (between clicks)

e. There are no bubble splits or additions as the bubbles flow past reagent injection manifolds.

Note: Air may also come through reagent lines if the lines is not down in the solution, or there are leaks or cracks in the connections.

2. If the bubble pattern is unacceptable after setting phasing with strike:

a. Check the surfactant levels in the appropriate reagents and start up solutions. Too little surfactant increases friction and drag on bubbles that may split them. This also increases back pressure problems that keep the bubbles our of phase and possibly irregularly spaced.

b. Check for back pressure problems from

(1) Clogs in the lines from particles and kinks in tubing

(2) Clogs in flow cell or waste lines

(3) Incorrect size of poly tubing used in lines.

To isolate where a clog or kink is, while system is running disconnect one section at a time starting from flow cell drain and working back. When pressure is relieved, there will be a notable surge in flow. Clean or replace the part of the sample line involved.

c. Adjust the length of tubing

(1) On the air line to the manifold, try different length and diameter poly tubing to help balance pump strength against line pressure. Sometimes a yellow-orange pump tube works well in this spot.

d. If bubbles are split at the reagent injection points, verify that manifold is not defective by replacing it with a new one.

J. Calibrate the chart record and monitor the baseline on start up solutions

1. Turn the chart recorder switch "on"

2. Remove the cap from the pen (connected to channel)

3. Lower the pen to the paper

4. Verify that the chart speed is set a 1 cm/min and going in down direction

5. On the computer, press [ENTER] till the Primary Commands are displayed. Select E: Utility Programs

6. Under Utility Programs, select 3: Scale

   a. Enter sample designator: A

   b. Enter "5" volts and verify pen has gone full scale to 5 volts on chart. If low or high, adjust with calibration (var/cal) knob on appropriate pen.

   c. Enter "0" and verify pen has gone to "0". If not, adjust with ⋖○⋗ knob on recorders.

   d. Recheck "5" and "0" volts to verify they are both in, then check other voltages. (Ex. 2.5, 0.25, etc.)

   e. Press [ENTER] again without a voltage and the program will go to "sample" and the chart recorder will directly monitor the voltage off of the spectrophotometer.

   f. If baseline is not smooth, check

      (1) Quality of start up solutions
      (2) If all unnecessary air is out of the system
      (3) Light source is on
      (4) Fiber optic end in flow cell holder is clean and flow cell holder is secure for sample and reference
      (5) Flow cell is clean
      (6) Bubble pattern is good and consistent
      (7) Bubble gate delay switch is in correct position
      (8) Bubble gate delay is adjusted*

      Note: Bubble gate delay determines what time, after a bubble passes through the flow cell, the spec will make a reading. The best theoretical time is 6/10 of a second. Adjust gate delay screw verifying that indicator light on top of spec flushes between passing bubbles. Then use baseline to

fine-adjust, making as smooth as possible. Noise must be eliminated sufficiently to discern a detection limit of 0.1 mg/L.

K. Run reagents and monitor baseline

Add the reagents one at a time to the system and if there is a noticeable increase in noise, filter or remake the reagent.

Note: A rise in voltage of baseline is normal

L. Initial spectrophotometer setup

1. After all reagents are in the system and an acceptable baseline is achieved, put the spectrophotometer function switch in the "sample" position. The voltage displayed is for the sample flow cell only. Use the sample gain controls to adjust the voltage to read 5.00 volts.

2. Put the function switch into the "absorbance" position. The voltage displayed is the comparative difference between the sample cell and the reference cell (the reference cell must be tightened so as not to vibrate). Adjust the reference gain controls to bring the voltage to 0.25 volts. Monitor the baseline as in step F to verify the chart recorder is also reading 0.25 volts, and that there is no drift across time. If there is a baseline drift, check the stability of the sample and reference flow cell to see that there are no leaks around the flow cells. Other causes for drift could be reagent quality and the sampler wash reservoir cleanliness. Once a stable baseline is achieved and the voltage is adjusted to a 0.25, make a dwell determination.

M. Determine Dwell Time

1. Place a sample cup containing high range standard 6 in the sampler tray and place tray on the sampler in the position for the cup to be sampled.

2. From the Primary Commands menu, select E: Utility Program commands

3. When you press the [ENTER] key, the following prompt will appear:

Enter Sample Designator (A/B) >

4. Enter "A" or "B" to indicate which sample (and Analytical Configuration File) you want to determine dwell times for, or simply press [ENTER] to abort the sequence. In either case, the program will return to the Menu E display. Meanwhile, if you entered a valid sampler designator, the sampler probe will sample from the dwell cup for the sample time in effect for the sampler, and

signals from all active data channels for the sampler will be displayed to the system strip chart recorders.

5. When the peak from the dwell sample appears in the signal on each data channel, the system will wait for the failing edge of the peak and then send the strip chart pen for that channel to zero. At the same time the message

   Channel N: Dwell Found, Dwell Time = XXX Seconds

   will be displayed in the real time message window on the CRT. When you see this message, you may have the dwell time value displayed by again entering "1" at the Menu E display to activate the Determine Dwell Times utility. The program will now display the following message and prompt.

6. **There are Dwell Times in the Queue**
   Print Hard Copy (Y/N)?

   Enter "Y' if you want to have the dwell times printed on the printer. Otherwise, enter "N" or just press the [ENTER] key. All dwell times in the queue will then be displayed on the CRT in the format shown below. If you selected hard copy, the same information will be printed on the printer. All values displayed are in seconds.

Channel Number	Dwell Time
N	XXX
M	YYY

Press Return to Continue

N. Readjust the spectrophotometer calibration

Once the high standard peak height is observed on the chart recorder from the dwell determination, adjust the calibration control to allow the high standard peak height to measure 90 to 95% across the 5 volt scale. After the calibration has been adjusted, readjust the spectrophotometer to a baseline of 0.25 volts as in Step L.

O. Modify the Analytical Configuration File (ACF)

1. To modify the ACF with "4" in response to the Menu "B" display. The program will prompt for a file name as follows:

   Enter Filename >
   Enter <Ammonia> as the filename

Do you wish to add/delete channels (Y/N)?>
Press [ENTER] to decline, then press [ENTER] until the frame with the dwell time is displayed. At this frame, enter "M" for modify. A series of prompts will display which is declined by [ENTER]. Proceed through the prompts until the dwell time prompt at which "Y" is entered. The prompt will then request the new dwell time to be entered at which the recent dwell determination in seconds will be entered.

Enter "E" to exit the sequence and respond to the following prompt.

Save modified file (Y/N)? >
Enter "Y"

Enter New Filename>
Press [ENTER] to maintain the old filename

Do you want to activate this file (Y/N)?
Enter "Y" to activate the file

P. Prepare the sample tray according to the Sample Identification File.

1. Fill each 2 mL cup completely.

2. Filter turbid sample cups with a 0.45 micron in-line polyethylene filter connected to a 10 cc syringe.

3. Place the completed tray on the sampler with cup #1 in position to be sampled when the run begins. Press the "reset" button on the sampler to ensure the tray is in the correct position.

Q. Inspect the reagents and the chart paper on the chart recorder to ensure there are sufficient quantities of both to supply the entire run.

R. Start the sample run.

1. Return to the Primary command and enter "C". Run samples in response to **the Waiting For Command >** prompt.

2. Select "1: Run" from the C menu and respond to the following prompts:

Enter Sample Designator (A/B) >
Enter "A"

Enter Sample ID Filename >

Enter the 8-digit sample identification file name created in section D.7.

Do You Wish to Collect Raw Data (Y/N) >
Enter "Y" to the prompt. A raw data file will be created and preserved for the run.

Enter Operator Initials >
Enter the analyst ID or name

Ready to Run (Y/N) >
When "Y" is entered at the prompt, the sampling begins, so be sure the system is completely ready to start. The peak heights will be monitored and displayed on the computer screen automatically unless [ENTER] is pressed at **the Press Return to Stop Monitoring >** prompt.

If the run is aborted or warning and error messages are displayed, reference the Alpkem manual for trouble shooting those problems.

S. Rerunning Samples

If peak heights are over range or distorted due to matrix or a sampling problem, reruns may be added to the end of the run as long as the sampler hasn't reached the last cup on the run by responding to the following prompts:

Enter "3" in response to the Menu C display.

Enter Sampler Designator >
Enter "A"

Enter Cup Number>
Enter the number of the cup to be redetermined. The program will repeat this prompt until pressing [ENTER] or until 40 cup numbers have been entered. The same cup number may be entered more than once to redetermine the same sample at different dilutions.

Cup Y Redetermination of X Enter Dilution Factor "NNNNN" >
The program repeats this prompt for each cup that is added to the run. In this line, "X" represents the original cup number and "Y" is the new cup number being added to the run. NNNNN is the sample identifier for "X" being assigned to "Y" prefixed with an ampersand (&) to indicate on the report that it is a redetermination. Enter any number up to 10 characters in length to indicate any dilutions or simply press [ENTER] if no dilution is being made. When all prompts for dilutions have been responded, the program will

automatically update the Sample Identification File and the sampler stop count and return to menu display.

Note: This entire entry sequence must be completed and the program returned to menu c before the system will recognize the request to run additional samples.

Prepare the additional sample cups using the dilutions indicated above and placing them in the correct positions on the sampler tray.

T. Obtaining Results

1. Select Menu **D: Print Hard Copy Commands** from the Primary Commands, then select *1: Plateau Data File* and respond to the following prompts:

   Enter Filename >
   Enter the 8-digit number used to create the Sample ID file for the run. Then select 1: Final Results from the menu displayed

   Suppress Flags on Report (Y/N)? >
   Enter "Y" unless the flags explained in Appendix C of the Alpkem manual are useful in evaluating the data.

   Redirect Printer Output (Y/N)? >
   Enter "N" to this prompt unless it is helpful to preview the report on the computer screen before the report is printed. The printer will begin printing the results immediately after "N" or will display the Plateau Data Reports menu again.

Before turning system off, run DI water through the system and all reagent lines for 15 minutes. After turning the systems off, remove all platens and release pump tube pressure from the pump rollers.

XIV. CALCULATIONS:

$$\frac{A \times B \times C}{D} = mg/L \text{ as } N$$

Where:

A = Alpkem results
B = Color dilutions taken
C = Final volume after distillation
D = Initial sample aliquot

XV. QA REQUIREMENTS

A. Method Blank: A DI water blank taken through the entire procedure with every 20 samples. The acceptance criteria is < 0.1 mg/L.

B. Laboratory Control Standard (LCS): A mid range standard taken through the entire procedure with every 20 samples. The acceptance criteria is determined by statistical control limits.

C. Calibration Blank: A blank of the same matrix as the standards that is analyzed during the color development to demonstrate system cleanliness and baseline stability.

D. Calibration Standards: A series of standards including a detection limit, a mid range and a high range. The acceptance range of these standards is a correlation coefficient of ≥ 0.995. The standards must have the same identification and concentration as described in the Analytical Configuration File and are denoted on the sample identification file with a pound sign (#).

E. Independent Calibration Verification Standard (ICV): A mid range standard prepared with the calibration standards but from an independent source to show the accuracy of the calibration standards. An independent source would be defined as a different chemical a different manufacturer or a different manufacturer's lot number. The acceptance criteria for the ICV is ± 10% of the theoretical value.

F. Duplicate: A duplicate sample analysis will be done through the entire procedure with every 10 samples with an acceptance criteria of a relative percent difference (RPD) of ≤ 20%.

G. Matrix Spike: A spiked sample will be analyzed through the entire procedure with every 10 samples. The acceptance criteria is a matrix spike recovery (MSR) of ± 25 % of the theoretical value.

H. Continuing Calbration Verification (CCV): A mid range calibration standard will be analyzed after every 10 samples. The acceptance criteria ± 10% of the theoretical value.

I. Continuing Calibration Blank (CCB): A blank of the same matrix as the standards that is analyzed after every 10 samples to demonstrate system cleanliness and baseline stability. The acceptance criteria is < 0.1 mg/L.

XVI. REFERENCES

A. Alpkem method number A303-5020-06

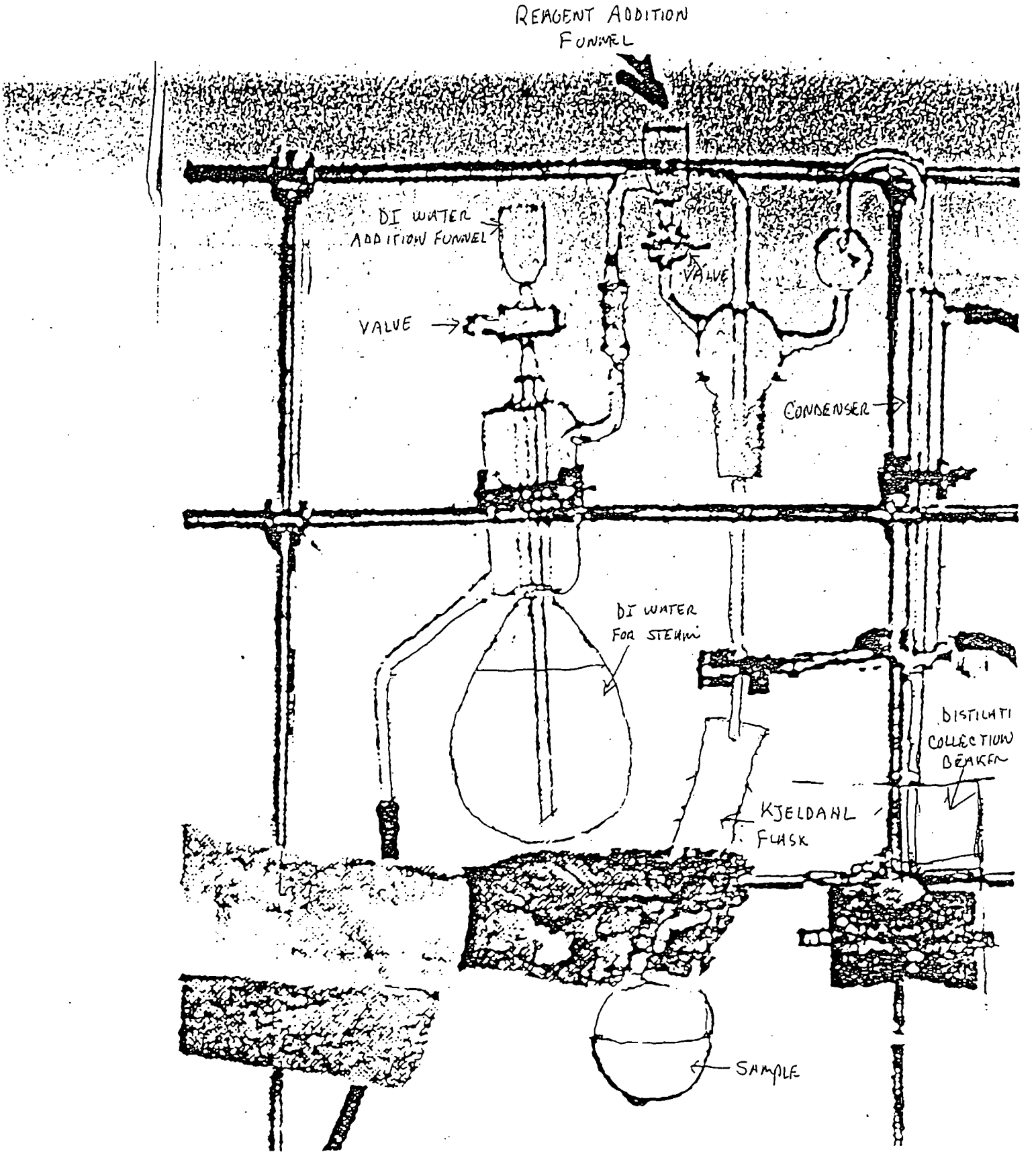
B. Methods for Chemical Analysis of Water and Wastes, March 1984, EPA-600/4-79-020, "Nitrogen, Ammonia" Method 350.2 (Colorimetric, Automated Phenate) STORET NO. Total 00610, Dissolved 00608.

XVII. EXHIBITS

A. Exhibit A - Apparatus Diagram

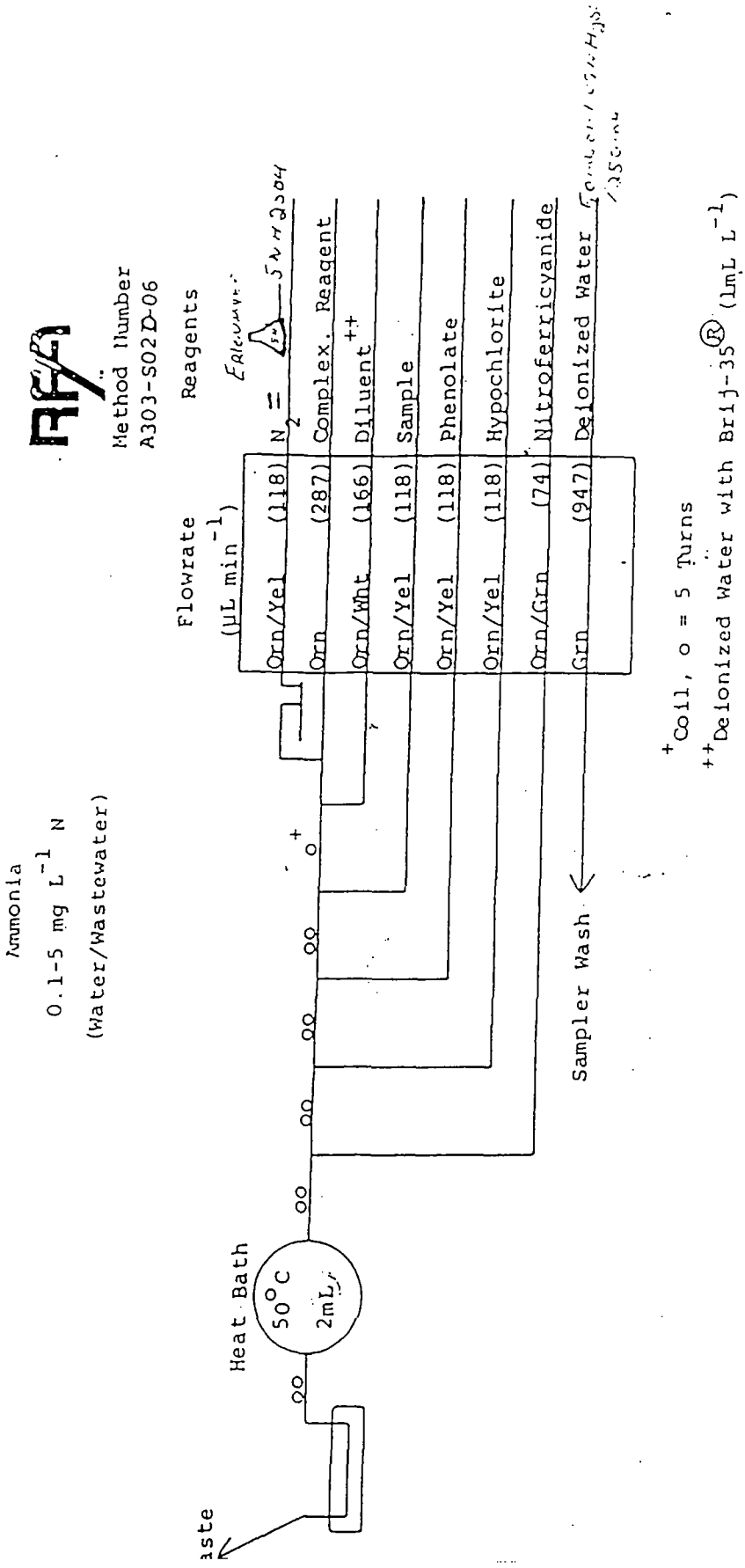
B. Exhibit B - Alpkem Operating Procedure Method A303-SO2O-06©

Exhibit A - Apparatus Diagram



PACE ANALYTICAL SERVICES, INC.

Exhibit B - Alpkem Operating Procedure Method A303-SO2O-006©



PACE ANALYTICAL SERVICES, INCORPORATED
HOUSTON LABORATORY

STANDARD OPERATING PROCEDURE

Separatory Funnel Extraction of Aqueous Samples for Organochlorine pesticides/PCB's

SOP NUMBER	HO-O-014-A
AUTHOR	Eddie Clemons
Effective Date	January 1, 1996
Supersedes	First Issue

APPROVAL

Department Supervisor — Date: 6/20/96

Quality Assurance Officer — Date: 6/21/96

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SEPARATORY FUNNEL EXTRACTION
OF AQUEOUS SAMPLES FOR
ORGANOCHLORINE PESTICIDES/PCB's

I. Purpose and Applicability

This procedure is based on SW-846 method 3510B and is used by organic preparation technicians to extract organic compounds from aqueous samples such as surface waters, groundwaters, and discharge waters. The separatory funnel extraction process used ensures intimate contact of the sample matrix with the extraction solvent. Sample extracts prepared by this method will be analyzed for organochlorine pesticides/PCB's.

II. Safety

This procedure requires the use of materials when handled improperly pose potential health risk to everyone in the laboratory. It is important that all necessary safety precautions are followed. This includes the use of properly operating fume hoods, appropriate gloves, protective eyewear, lab coats, and respiratory protection as necessary. Users of this procedure must be cognizant of inherent syringe and sonicator hazards, proper disposal procedures for contaminated materials, and appropriate segregation of waste. Everyone involved in the procedure must be familiar with the MSDS for solvents and chemicals used. Any additional information can be received by consulting with your chemical hygiene member.

III. Responsibility

A. Personnel

1. All personnel involved with sample preparation and analysis are responsible for adherence to this Standard Operating Procedure (SOP).

2. Personnel are responsible for ensuring that any deviations to this SOP are reported.

3. All personnel are responsible for notifying the department manager/supervisor of any required revisions to the SOP.

B. Department manager/supervisor

1. The department manager/supervisor is responsible for ensuring adherence to this SOP.

2. The department manager/supervisor is responsible for performing an annual review of the SOP and reporting any required revisions to the Quality Assurance Office.

C. Quality assurance office (QAO)

1. The QAO is responsible for conducting semi-annual laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Regional Management and Corporate Quality.

2. The QAO is responsible for ensuring that all revisions to the SOP are implemented.

3. The QAO is responsible for determining distribution of and maintaining document control for this SOP.

IV. **Reviews/revisions**

A. This SOP will be reviewed on an annual basis at a minimum.

B. At the time of review, any required revisions will be incorporated.

C. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

V. **Distribution**

This SOP will be issued to the Lab Manager, Corporate QAO, Regional QAO, and any other areas deemed appropriately Regional QAO.

VI. **Sampling Handling, Storage and Preservation**

All samples to be extracted under this SOP should be collected into 1000 mL glass containers with Teflon lined caps. Samples should be chilled to 2-6°C, and shipped to the lab. Samples should be stored at 2-6°C until extraction. No chemical preservatives should be added to the sample at the time of collection. Extraction must occur within 7 days of collection.

VII. **Materials and Apparatus**

Zymark TurboVap II solvent concentrator
TurboVap tubes
250 mL Erlenmeyer flasks
Nitrogen blow-down apparatus for concentrating extracts
Pasteur pipettes 1 ml
Methylene Chloride, pesticide grade
Hexane, pesticide grade
Sodium Sulfate, reagent grade heated at 400°C for 4 hours
Methanol, pesticide grade
Acetone, pesticide grade
Surrogate Standard Solution: Surrogate is made from a commercially purchased solution of TCMX and DCB and diluted to yield a final concentration of 1.0 ug/mL of each in acetone.
Spike Solution: Prepare a control spike standard solution in acetone with the analytes at the concentrations listed in Table I.
Multiresponse Analyte Spike Solution: Prepare control spike standard solutions in acetone of each multiresponse analyte at the concentrations listed in Table II.
2 liter separatory funnel
Graduated cylinder
pH paper
Mechanical shaker(optional)
1:1 sulfuric acid: prepare by adding 100 ml concentrated sulfuric acid to 100 ml DI water in an ice jacket
10M sodium hydroxide: prepare by adding 40 g of sodium hydroxide to 100 ml of DI water
Timer/ stopclock

VIII. **Definitions**

ANALYTICAL BATCH: A group of samples numbering twenty or less which are extracted together under the same sop using the same lots of reagents and with the manipulations common to each sample within the same time period.

LABORATORY REAGENT BLANK (METHOD BLANK): A blank sample designed to determine if method analytes or other interference's are present in the laboratory environment, the reagents, or the apparatus. For aqueous

samples, deionized (DI) water is used as a blank matrix. The blank is taken through the appropriate steps of the process. A method blank should be extracted daily or with every analytical batch of samples.

LABORATORY CONTROL SAMPLE (LCS): A blank which has been spiked with the analyte(s) from an independent source and is extracted exactly like a sample. Its purpose is to determine whether the methodology is in control. An LCS is extracted daily or with every analytical batch of samples.

MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD): A selected sample is split into three replicates. Two of the replicates are spiked with the analyte(s) from an independent source and is extracted exactly like the third replicate and the other samples. Percent recoveries are calculated for each of the analytes detected in the MS and the MSD. The relative percent difference between the MS and the MSD is calculated and used to assess analytical precision.

SURROGATES: Organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, standards, samples, and spiked samples prior to extraction. Percent recoveries are calculated for each surrogate in each sample.

IX. Quality Control

One LCS and method blank should be prepared daily, every 20 samples or less or with every analytical batch, whichever occurs first.

Matrix spike and matrix spike duplicates are extracted every 20 samples, once per month, when requested by the client, or to meet project specific requirements.

X. Sample Extraction

A. Ascertain that all glassware is clean and dry. Thoroughly rinse all glassware used with methylene chloride before proceeding with extractions.

B. Assign a method blank, and lab control sample to a batch of twenty samples or less. Record in the extraction log book.

C. Set up a 2 liter separatory funnel with stopcock and stopper, and a TurboVap concentrator tube for each sample. NOTE: All containers used to collect samples must be individually labeled; i.e. separatory funnels, concentrator tube, etc. If an Erlenmeyer flask is used, add 10 mL of sodium sulfate to the flask. Prepare a sodium sulfate filter funnel by placing fluted filter paper in a large glass funnel and filling to a depth of 2-3 cm with sodium sulfate. Using a wash bottle, rinse the funnel and contents 3 times with 10-15 ml of methylene chloride and let drain into a chlorinated solvent waste container. Place funnel on top of TurboVap concentrator tube.

D. On a 1 liter or less sample container clearly mark the sample meniscus, and add approximately 1 liter of sample to each separatory funnel. If a smaller aliquot of sample is used dilute the sample with DI water to a final volume of 1000 mL. NOTE: The total volume extracted must be 1000 mL. If the sample matrix

appears to be wholly or partially oil, contact your supervisor before proceeding.

E. Unless otherwise specified, DI water will serve as the method blank and LCS. For each blank and LCS measure and add 1 liter of DI water to a separatory funnel.

F. Use pH paper to check the pH of each sample prior to beginning extraction. The pH should be neutral (5-9). If the pH is outside the range note the pH in the logbook.

G. Using a syringe, add 1.0 mL of Spike Solution listed in Table I to the LCS, MS/MSD. Extreme accuracy should be used when measuring and adding the spike solution. Rinse the syringe with methanol before and after use. NOTE: When the samples are to be analyzed only for one or more of the multiresponse analytes add 1.0 mL of the specific multiresponse Spike Solution listed in Table II. Separate LCS and MS/MSD samples must be prepared when more than one of the spike solutions are needed since there are analytical interference's when they are present in the same extract.

H. Using a syringe, add 1.0 mL of the Surrogate Solution to all samples including blank, LCS, and MS/MSD. Extreme accuracy should be used when measuring and adding the surrogate solution. Rinse the syringe with methanol before and after use.

I. Add 60 ml of methylene chloride to the separatory funnel.

J. Shake and vent each funnel under a hood until there is no more pressure build-up. Vigorously hand shake or place on mechanical shaker for 2-3 minutes.

K. Allow the organic layer to separate from the water phase for approximately ten minutes. Swirl the separatory funnel several times to drop any methylene chloride floating on the surface.

L. If an emulsion layer is not present, drain the organic layer (bottom) into the appropriate TurboVap tube.

M. If an emulsion layer is present, drain into a labeled beaker with sodium sulfate and using a glass stir rod stir until emulsion layer disappears. Pour sample through filter funnel into TurboVap concentrator tube.

N. Repeat extraction (steps I-M) twice more with additional 60 mL portions of methylene chloride and cover each flask. NOTE: All three portions of extract should be combined into one concentrator tube.

O. Rinse the filter with an additional 15-30 mL of methylene chloride and let drain.

P. After draining, dump solids and filters into the disposal container and let dry under hood. Discard when dry.

Q. Measure the sample volume extracted by draining the sample into a 1000mL graduated cylinder. Record the volume in the extraction log to the nearest 5 mL.

R. Set up the TurboVap in accordance with manufacturer's instructions. Place TurboVap tubes in TurboVap and close door. Concentrate the sample to 1-5 mL. Do not concentrate the extract to dryness.

S. Remove the TurboVap tube from the TurboVap and add 50mL hexane. Return the tube to the TurboVap and concentrate to 1-5 mL. This will exchange the solvent from methylene chloride to hexane. Do not concentrate the extract to dryness.

T. Remove the TurboVap tube from the water bath and allow to cool. Transfer the sample into a labeled sample vial and rinse the sides of the TurboVap tube with 1-5 mL of hexane. Transfer the rinsate into the sample vial. Adjust the extract volume to 10mL.

U. Filter extracts only if there are visible particulates in the extract using 0.45 µm Millex Filters.

V. Record the final extract volume in the extraction log.

W. The extract is now ready for analysis. Record the sample initial volume, aliquot volume and final volume in the logbook. Verify that the surrogate and spike solutions identification numbers and amounts used have been recorded. Any deviations from this SOP or abnormal sample observations should be noted in the logbook.

XI. Calculations/Reporting

Information relevant to each extraction must be entered into the laboratory extraction logbooks.

XII. Applicable Documents/References

Test Methods for Evaluating Solid Waste Physical/Chemical Methods, US EPA SW 846, 3rd edition: Method 3510B.

TABLE I

Spike Solution Concentration Levels
(mg/L)

Pesticides	Level
alpha-BHC	1.0
beta-BHC	1.0
delta-BHC	1.0
gamma-BHC (Lindane)	1.0
Heptachlor	1.0
Aldrin	1.0
Heptachlor Epoxide	1.0
Endosulfan I	1.0
Dieldrin	1.0
4,4'-DDE	1.0
Endrin	1.0
Endosulfan II	1.0
4,4'-DDD	1.0
Endrin Aldehyde	1.0
4,4'-DDT	1.0
Endrin Ketone	1.0
Methoxychlor	1.0

TABLE II

Spike Solution Concentration Levels
for
Multiresponse Analytes
(mg/L)

Pesticides	Level
Aroclor 1242	10
Toxaphene	5
Chlordane	5

PACE ANALYTICAL SERVICES, INCORPORATED
HOUSTON LABORATORY

STANDARD OPERATING PROCEDURE

1,2-Dibromoethane (EDB) And 1,2,3-Trichloropropane (1,2,3-TCP) By Microextraction and Gas Chromatography

SOP NUMBER	HO-O-028
AUTHOR	Matt Hearne
Effective Date	January 21, 1997
Supersedes	First Issue

APPROVAL

Russell Morgan — Department Supervisor — 1/23/97 — Date

Quality Assurance Officer — 1/23/97 — Date

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1,2-EDB And 1,2,3-TCP
by Microextraction and Gas Chromatography

I. Purpose and Applicability

Method 8011 is used to determine the concentration of various chlorinated and brominated organic compounds for evaluating drinking water and ground water samples in compliance with RCRA regulations.

II. Summary of Method

Thirty five mL of sample are extracted with 2mL f hexane. Two uL of the extract are then injected into a gas chromatograph equipped with a linearized electron capture detector (ECD) for separation and analysis. Aqueous matrix spikes are extracted and analyzed in an identical manner as the samples in order to compensate for possible extraction losses. The method provides optional GC operating conditions and GC column that may be helpful in resolving the analytes from co-eluting non-target compounds and for analyte confirmation.

III. Interferences

This SOP may be used to analyze water/ liquid matrices. The working range for this SOP is 0.03 - 200 ug/L. Actual detection limits are highly dependent upon the characteristics of the gas chromatographic system, sample matrix, and calibration. Impurities contained in the extracting solvent (hexane) usually account for the majority of the analytical problems. Reagent blanks should be analyzed for each new bottle of hexane before use. Method blank prepared from organic-free reagent water extracting solvent (hexane) can serve as a check for such contamination. Accidental sample contamination have been attributed to diffusion of volatile organics through the septum seal into the sample bottle during shipment and storage. Trip blanks must be used to monitor for this problem.

IV. Safety.

This procedure requires the use of materials, which when handled improperly, pose potential health risk to everyone in the laboratory. It is important that all necessary safety precautions are followed. This includes the use of properly operating fume hoods, appropriate gloves, protective eyewear, lab coats, and respiratory protection as necessary. Users of this procedure must be cognizant of inherent syringe hazards, proper disposal procedures for contaminated materials, and appropriate segregation of waste. Everyone involved in the procedure must be familiar with the MSDS for solvents and chemicals used. Any additional information can be received by consulting with your Chemical Hygiene Plan.

V. Responsibility

A. Personnel

1. All personnel involved with sample preparation and analysis are responsible for adherence to this Standard Operating Procedure (SOP).

2. Personnel are responsible for ensuring that any deviations to this SOP are reported.

3. All personnel are responsible for notifying the department manager/supervisor of any required revisions to the SOP.

B. Department manager/supervisor

1. The department manager/supervisor is responsible for ensuring adherence to this SOP.

2. The department manager/supervisor is responsible for performing an annual review of the SOP and reporting any required revisions to the Quality Assurance Office.

C. Quality assurance office (QAO)

1. The QAO is responsible for conducting periodic laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Regional Management and Corporate Quality.

2. The QAO is responsible for ensuring that all revisions to the SOP are implemented.

3. The QAO is responsible for determining distribution of and maintaining document control for this SOP.

VI. Reviews/revisions

A. This SOP will be reviewed on an annual basis at a minimum.

B. At the time of review, any required revisions will be incorporated.

C. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

VII. Distribution

This SOP will be issued to the GC lab and any other areas deemed appropriate by the QAO.

VIII. Equipment and Supplies

A. Gas chromatograph: Varian 3400 or equivalent analytical system complete with all required accessories and data system.

B. Columns:
Column 1 -30m x 0.53mm, 3.0 micron, RTX-5 or equivalent
Column 2 -30m x 0.53mm, 3.0 micron RTX-1701 or equivalent

C. Detectors - 2 Electron Capture detector (ECD).

D. Microextraction and direct injection of Sample, refer to sec.7.4 of this method.

E. Syringes, Microsyringe, 10, 25 and 100 ul (hamliton 702N or equivalent).

F. Reagents:
All chemicals and solvents should be reagent grade or better shall be used in all tests.
Organic-free reagent water as defined in SW846 chapter one.
Hexane, UV grade or equivalent.

IX. Sample Preparation

A. Remove samples and standards from storage and allow them to reach room temperature.

B. For samples and field blanks contained in 40 mL bottles, remove the container cap. Discard a 5 mL volume using a 5 mL transfer pipet. Replace the container cap and weigh the container with contents to the nearest 0.1 g and record this weight for subesequent sample volume determination.

C. For calibration standards, check standards, QC reference samples, and blanks, measure a 35 mL volume using a 50 mL graduated cylinder and transfer it to a 40 mL sample container.

D. Extraction

1. Remove the container cap and add 7 g of NaCl to all samples.

2. Recap the sample container and dissolve the NaCl by shaking by hand for about 20 seconds.

3. Remove the cap and using a transfer pipet, add 2.0 mL of hexane. Recap and shake vigorously by hand for 1 minute. Allow the water and hexane phases to separate. If stored at this stage, keep the container upside down.

4. Remove the cap and carefully transfer a sufficient amount (0.5-1.0 mL) of the hexane layer into a vial using a disposable glass pipet.

5. Transfer the remaining hexane phase, being careful not to include any of the water phases, into a second vial. Reserve this second vial at 4°C for reanalysis if necessary.

6. Transfer the first sample vial to an autosampler set up to inject 2.0 µL portions into the gas chromatograph for analysis. Alternately, 2 µL portions of samples, blanks and standards may be

manually injected, using the solvent flush technique, although an autosampler is strongly recommended.

X. Standards

Sources: NSI, Protocol, Supelco, Chem Service or equivalent

The purchased certified stock standard solutions in methanol can contain some or all compounds of interest, either singly or mixed together at a concentration of 5000ug/ml (See Table 1). The secondary standard dilution should be prepared at concentrations such that the calibration standards will bracket the working range of the analytical system. Secondary standards should be stored with minimal headspace for volatile compounds and should be checked frequently for signs of degradation or evaporation.

5000(ug/ml) * 0.01(ml)/10(ml MeOH) = 5000(ng/ml) Primary stock conc
5000(ng/mL) * 0.1(ml)/5(ml MeOH) = 100(ng/mL) Secondary stock conc.

XI. Calibration Standards

Prepare calibration standards in organic-free reagent water, from the secondary stock std, at a minimum of five concentrations. One of the concentrations should be near, but above, the method detection limit (MDL). The remaining concentrations should correspond to the working range of the GC. The following standards are recommended for this method:

Std level	(X)ul/10ml water	Conc. (ug/L)
1	3	0.03
2	5	0.05
3	10	0.10
4	15	0.15
5	20	0.20
6	30	0.30

Aqueous working standards are not stable and should be discarded after eight hour, unless properly sealed and stored. The aqueous standard can be stored up to 24 hours, if held in sealed vials with zero headspace.

Ex. Calculation: (10 ul x 100ug/L)/10ml = 0.10ug/L Final Conc.

XII. Calibration

The external standard calibration procedure is used. Each analyte of interest is run at a minimum of 5 different concentrations and a calibration curve is constructed. Results will be obtained from the

curve. If the %RSD of the calibration factor for each component is less than 10%, linearity through the origin can be assumed, and the average calibration factor can be used. The concentration of the calibration standards should define the working range of the instrument. See Figure 1 for an example of a typical calibration sequence including concentrations. See Figures 1a-1d for retention time orders and example chromatograms.

Daily continuing calibrations are analyzed at a concentration of 0.10 ug/L and must fall within the limits posted in Table 3 under "Range for Q". If any analyte of interest fails these criteria, then all samples that require the failing compound analyzed after the failing calibration must be reanalyzed.

Midpoint calibrations must be verified every 20 samples and must fall within 15% of the concentration level. If any analyte of interest fails these criteria, then all samples that require the failing compound analyzed after the failing calibration must be reanalyzed. On a daily basis, the laboratory must demonstrate the ability to analyze a Laboratory Control sample, LCS (0.10ug/L).

XIII. Retention Time Windows

Whenever a new column is installed into the GC, retention time windows must be established. The windows are initially established by monitoring and recording the retention times of the peaks. The data are collected from three separate injections of standards over a 72 hour period of time. The retention time window is calculated as plus or minus three times the standard deviation of the retention time for each peak. For compounds that have standard deviations of retention time that are extremely small, the retention time window from a compound that it is close to, and similar with, should be substituted.

For daily analysis, the absolute retention time from the standards run within that 24 hour period of time will be used as the midpoint of the window. Tentative identification of target compounds will be based on peaks that elute during the daily retention time window and the chromatogram produced by the detector and computer system.

XIV. Analytical Sequence

Table 2 shows a typical sequence of analysis beginning with an initial calibration, sample analyses, and continuing calibration, and closing calibration.

XV. Quality Control

A. Method Blanks

A method blank is prepared and analyzed with every batch of up to 20 samples extracted. If any target compounds are detected in the method

blank at or above the reporting limit, all samples with positive hits for those compounds must be re-extracted.

B. LCS Recoveries
A Lab Control Sample (LCS) prepared from a source separate from the calibration standards is run with every extracted batch of samples. The LCS control limits are calculated from historical data. If the LCS results are outside the control limits, corrective action must be taken. The analyst should first check the instrument performance, followed by reanalysis of the LCS. For analytes that do not have enough historical data, use the limits in Table 3 under "Range P, P_S %"

D. MS/MSDs
A matrix spike and matrix spike duplicate are extracted at a 5% frequency or as specified by the project. If the recovery of any compound spiked does not fall within the control limits established for the LCS, that compound must demonstrate acceptable recovery in the associated LCS, and the data flagged as indicative of possible matrix interference.

XVI. Applicable Documents/References

Test Methods for Evaluating Solid Waste Physical/Chemical Methods, US EPA SW 846, 3rd edition: Method 8011.

TABLE I
Calibration Standards

Standard Compounds:	R.T.(min) Col: A	R.T.(min) Col: B	conc. (ug/L)
1,2-EDB	3.92	4.67	100
1,2,3-TCP	5.23	6.51	100

TABLE II
Calibration and Analytical Sequence

System Blank (Hexane)
8011 Std. (level #1)
8011 Std. (level #2)
8011 Std. (level #3)
8011 Std. (level #4)
8011 Std. (level #5)
LCS (0.10ug/L)
Samples (20 total)
8011 Std. (mid-pt calibration level)
Samples (20 total)

Note: Method Blanks, LCS's, MS/MSD's are included in the total of 20 samples between calibration checks; instrument blanks are not. Calibration check standards must be analyzed at a minimum every 24 hours of sample analysis.

Table III
Single Laboratory Accuracy and Precision
for EDB and 1,2,3-TCP

Analyte	Number of Samples	Spike Conc. (ug/L)	Average Recovery (%)	Relative Standard Deviation
EDB	7	0.28	104	0.0009
1,2,3-TCP	7	0.28	110	0.022

STANDARD OPERATING PROCEDURE

Chloride - Alpkem Colorimetric Determination

SOP Number	HO-I-033
Author	Bruce Brown
Effective Date	January 15, 1997
Supersedes	First issue

Approvals:

Bruce Brown
General Chemistry Supervisor

1-23-97
Date

Russell Morgan
Laboratory Manager

1/23/97
Date

Quality Assurance Officer

1/23/97
Date

I. SCOPE AND APPLICATION

A. This automated method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

B. The applicable range is 2 to 100 mg Cl/L. This range may be extended by sample dilution.

II. SUMMARY OF METHOD

A. Thiocyanate ion (SCN) is liberated from mercuric cyanate through sequestration of mercury by chloride ion to form un-ionized mercuric chloride.

B. In the presence of ferric ion, the liberated SCN forms highly colored ferric thiocyanate in concentration proportional to the original chloride concentration.

C. The colored complex is measured at 480 nm.

III. INTERFERENCES

A. There are no significant interferences.

B. Filter turbid samples before determination.

IV. SAMPLE HANDLING AND STORAGE

A. No preservation is required.

B. The holding time for samples is 28 days.

V. SAFETY INFORMATION

Each chemical compound used in this SOP should be treated as a potential health hazard. Care should be used while handling samples because of toxicity. Exposure to these substances must be reduced to the lowest possible level by whatever means available (i.e., gloves, lab coats, eye protection, fume hoods). Reference files of OSHA regulations and Material Safety Data Sheets (MSDSs) are available to all personnel involved in this analysis.

VI. RESPONSIBILITIES

A. Analysts

1. All analysts performing this procedure are responsible for strict adherence to the SOP.

   Analysts are responsible flro ensuring that any deviations to this SOP are reported.

   Analysts are responsible for reporting to the section supervisor any required revisions to the SOP.

B. Department Supervisors/Managers

1. The department supervisor/manager is responsible for ensuring adherence to this SOP.

2. The department supervisor/manager is responsible for performing an annual review of this SOP and reporting any required revisions to the Quality Assurance Officer.

C. Quality Assurance Officer (QAO)

1. The QAO is responsible for conducting semi-annual laboratory audits ot monitor adherence to this and other SOPs. Results of the audit will be reported to Regional Management and Corporate Quality.

2. The QAO is responsible for ensuring that all revisions to the SOP are implemented.

3. The QAO is responsible for determining distribution of and maintenance of document control for this SOP.

VII. REVIEWS / REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. Required revisions will be incorporated at the time of the review.

C. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

VIII. DISTRIBUTION

Distribution of this SOP will be determined by the Quality Assurance Officer.

IX. APPARATUS

An Alpkem autoanalyzer equipped with a Chloride analytical cartridge, spectrophotometer with 480 nm filter, autosampler, chart recorder, and computer designed to run the system and produce a report of final results.

X. REAGENTS

A. Stock Mercuric Thiocyanate

1. Mercuric Thiocyanate $Hg(SCN)_2$ (FW 316.75)

2. Methanol

Dissolve 4.17 g of mercuric thiocyanate in approximately 500 mL of methanol contained in a 1L volumetric flask. Dilute the solution to the mark with methanol and mix well. Filter the solution through a medium paper filter.

Caution: Mercuric thiocyanate is a poison. Do not breathe dust. wash hands thoroughly after handling. Methanol is flammable Ingestion may be fatal or cause blindness. Avoid prolonged breathing of vapor. Use both materials only with adequate ventilation.

B. Stock Ferric Nitrate

Ferric Nitrate $Fe(NO3)3\ 9H2O$ (FW 404.00)

Nitric Acid $HNO3$, concentrated

Deionized Water

Dissolve 202 g of ferric nitrate in approximately 500 mL of deionized water contained in a 1L volumetric flask. Carefully add 31.5 mL of nitric acid. Dilute the solution to the mark with deionized water and mix it well. Filter through a medium filter paper.

C. Working Chloride Color Reagent (200 mL)

Stock Mercuric Thiocyanate

Stock Ferric Nitrate

Deionized Water

Add 30 mL of stock mercuric thiocyanate and 30 mL of stock ferric nitrate to approximately 100 mL of deionized water contained in a 200 mL volumetric flask. Dilute the solution to the mark with deionized water and mix it well.

D. Stock Nitric Acid

Nitric Acid $HNO3$, concentrated

Deionized Water

Cautiously add 15.8 mL of concentrated nitric acid to 800 mL of deionized water contained in a 1L volumetric flask. Dilute to the mark with deionized water.

E. Working Nitric Acid (100mL)

Stock Nitric Acid

Brij-35, 30 %

Add 0.1 mL of Brij-35 to each 100 mL of nitric acid used. Refer to flow diagram, this is used with manifolds containing dialyzer assembly.

XI. PROCEDURE

A. Instrument Set-up

1. Set the spectrophotometer and the autosampler to the following parameters:

   a. Spectrophotometer parameters:

Filter	480 nm
Flowcell	10 mm
Absorbance Range	0.5 AUFS
Damping	4s

   b. Autosampler parameters:

Analysis Rate	72/hr
Sample Time	20s
Wash Time	40s

2. Clean the platens and the pump rollers with isopropyl alcohol.

   a. Check the platens for excessive wear and replace them if necessary.

   b. the pump roller carriage may be turned by hand for access to all of the rollers to clean them after clearing the previous test tubing.

3. Install the appropriate board and reagent lines

   a. Retrieve the board from the drawer and carefully unwrap the reagent lines.

   b. Set the board into the module, bringing the reagent lines to drape on front of the module.

   c. Inspect the reagent lines and connections for wear, splits, cracks and solid clogs, and replace if necessary.

   d. Inspect the tubing for wear at the point of the pump roller crossing and replace them if misshapen and flattened.

   f. Inspect the mixing coils, manifolds and connectors for cracks, leaks or clogs, and replace or clean them as necessary.

   g. Inspect and install, as needed according to the Alpkem diagram, all the air lines, sample wash feed lines and waste lines.

   h. Connect the sample line the sample probe.

i. Position the reagent, sample, waste, sample wash and air line in an arrangement across the pump rollers so that

(1) both sides of each platen will have at least one line under it (use dummy lines if needed)

(2) the lines closest in size share a platen

(3) the lines have no sharp bends or kinks

(4) the lines all neatly go to their destinations with a minimum of confusion and tension.

j. Install the platens (if the unit is on, leave one unclamped to keep the pump from starting).

k. Place the reagent lines into DI water and/or the appropriate start up solution bottles.

4. Install the appropriate filters and the flow cell to the spec.

a. Select the appropriate filters according to the Alpkem diagram.

b. Wipe the filters with KimWipes and gently remove any particles of dust.

c. Screw the filters into the special housing (glass side in) until they are snug.

d. Select the appropriate flow cell according to the Alpkem diagram and inspect it for cleanliness (gently back flush with DI water if necessary using a syringe). Make sure the flow cell is completely dry after flushing it by wiping with a KimWipe.

e. Install the flow cell drain tube to the side of the flow cell closest to the spec and connect the other side of the flow cell to the flow cell feed line from the last mixing coil.

f. Gently install the flow cell to the sample side of the spec positioned between the filter and the light source. Tighten this snugly with an allen wrench. Install the reference cell to the reference filter and the light source; tighten this snugly with an allen wrench.

g. Place the flow cell drain tube and any other waste lines in the waste hole on the board.

5. Run the system on the appropriate start up solutions.

a. Verify that the front module switches oar on for the sampler, light source, and the pump module.

b. Clamp all of the platens down and turn on the system with the switch located on the master power supply box. The pump should immediately start. If not,

(1) Check that the platens are securely clamped

(2) Check that all the appropriate switches are on

(3) Check that all plugs into the master power supply box are securely tied in

(4) Turn off the system and check the fuse located in the master supply box.

c. Verify that the light source is illuminated, if not,

(1) Check the light source switch is on

(2) Check the light source plug to the power box

(3) Check the light source bulb by unscrewing the light source cable from the back of the module and replace if blown. WARNING - plug may be hot, insulate fingers with a paper towel.

d. Make initial spec settings

(1) Put the bubble gate switch on the side of the spec in the "on" position if not using a debubbler on the flow cell and "off" if one is used.

(2) Set the damping control on top of the spec to position indicated on Alpkem diagram

(3) Set the calibration control on top of spec to 1.50

(4) Allow the system to run until all the air is out of all lines and coils with evenly spaced bubbles going through the flow cell.

e. Adjust the bubble phasing to achieve an acceptable pattern (if a debubbler is not used on the flow cell)

(1) The bubble phasing control is a selector switch located in the back of the pump modules (ref. manual). Turning the switch allows preset adjustment of the phasing between the pumps downstroke and the valves injection of the bubble

into the manifold. The optimum theoretical setting is a bubble injection simultaneous with the pumps downstroke, but often something slightly different is what is required. Strokes are denoted with a click sound. Adjust the control so that the bubbles injected are:

Single - split bubbles are out of phase with stroke
Correct size and equal in size

Oval (not round) and regularly spaced

There are no intermediate bubbles (between clicks)

There are no bubble splits or additions as the bubbles flow past the reagent injection manifolds.

Note: Air may also come through reagent lines if the line is not down in the solution, or there are leaks or cracks in the connections.

f. If the bubble pattern is unacceptable after setting phasing with stroke:

(1) Check the surfactant levels in the appropriate reagents and start up solutions. Too little surfactant increases friction and drag on bubbles that may split them. This also increases back pressure problems that keep the bubbles out ot phase and possibly irregularly spaced.

(2) Check for back pressure problems from:

Clogs in the lines form particles and kinks in tubing

Clogs in flow cell or waste lines

Incorrect size of poly tubing used in lines

Note: To isolate a clog or kink, disconnect one section at time while the system is running. Start with the flow cell drain and work back. When pressure is relieved there will be a notable surge in flow. Clean or replace the part of the sample line involved.

(3) Adjust the length of tubing on the air in to the manifold. Sometimes different lengths and diameters of poly tubing balance line pressure to

pump strength.

(4) If bubbles are being split at the reagent injection points, verify that manifold is not defective by replacing it with a new one.

6. Calibrate the chart recorder and monitor the baseline on start up solutions

a. Turn the chart recorder switch "on"

b. Remove the cap from the pen (connected to channel)

c. Lower the pen to the paper

e. Verify that the chart speed is set at 1cm/min and going in down direction

f. On the computer, press [Enter] till the Primary Commands are displayed. Select E: Utility Programs

g. Under Utility Programs, Select 3: Scale

(1) Enter sampler designator: A

(2) Enter "5" volts and verify pen has gone full scale to 5 volts on the chart recorder. If low or high, adjust with calibration (var/cal) knob on appropriate pen.

(3) Enter "0" volts and verify pen has gone to 0 on chart recorder. If not, adjust with 0 knob on recorder

(4) Recheck "5" and "0" volts to verify they are both in, then check a mid-range volt such as 2.5.

(5) Press [ENTER] again without a voltage and the program will go to "sample" and the chart recorder will directly monitor the voltage off of the spec.

(6) If baseline is not smooth, check:

Quality of start up solutions

If all unnecessary air is out of the system

Light source is on

Fiber optic end in flow cell holder is clean and flow

cell holder is secure for sample and reference cells.

Flow cell is clean

Bubble pattern is good and consistent

Bubble gate delay switch is in correct position

Bubble gate delay is adjusted

Note: Bubble gate delay determines what time, after a bubble passes through the flow cell, the spec will make a reading. The best theoretical time is 6/10 of a second. Adjust gate delay screw verifying that indicator light on to of spec. flashes between passing bubbles. Then use baseline smoothness to fine adjust. Noise must be eliminated sufficiently to discern a detection limit of 1mg/L

7. Run reagents and monitor baseline

   Add the reagents one at a time to the system and if there is a noticeable increase in noise, filter or remake the reagent.

   Note: A rise in voltage of the baseline is normal

8. Initial Spectrophotometer set up

   a. After all reagents are in the system and an acceptable baseline is achieved, put the spec function switch in the "sample" position. the voltage displayed is for the sample flow cell only. Use the sample gain controls to adjust the voltage to read 5.00 volts.

   b. Put the function switch into the "absorbance" position. The voltage displayed is the comparative difference between the sample cell and the reference cell (the reference cell must be tightened so as not to vibrate). Adjust the reference gain controls to bring the voltage to 0.25 volts. Monitor the baseline as in step F to verify the chart recorder is also reading 0.25 volts, and that there is no drift across time. If there is a baseline drift, check the stability of the sample and reference flow cell to see that there are no leaks around the flow cells. Other causes for drift could be reagent quality and the sampler was reservoir cleanliness. Once a stable baseline is achieved and the voltage is adjusted to 0.25, make a dwell determination.

9. Determine dwell time

a. Place a sample cup containing highest range standard (see step 12) in the sampler tray and place the tray on the sampler in the position for the cup to be sampled.

b. From the Primary Commands menu, select E: Utility Program commands.

c. When you press the [ENTER] key, the following prompt will appear:

Enter Sample Designator (A/B) >

d. Enter "A" or "B" to indicate which sampler channel (and Analytical Configuration File) you want to determine dwell times for, or simply press [ENTER] to abort the sequence. In either case, the program will return to the Menu E display. Meanwhile, if you entered a valid sampler designator, the sampler probe will sample form the dwell cup for the sample time in effect for the sampler, and signals from all active data channels for the sampler will be displayed to the system strip chart recorders.

e. When the peak from the dwell sample appears in the signal each data channel. the system will wait for the falling edge of the peak and then send the strip chart pen for that channel to zero. At the same time, the message

Channel N: Dwell Found, Dwell Time = XXX Seconds

will be displayed in the real time message window on the CRT (cathode ray tube). When you see this message, you may have the dwell time value displayed by again entering "1" at the Menu E display to activate the Determine Dwell Times utility. The program will now display the following message and prompt.

f. **There are Dwell Times in the Queue**
Print Hard Copy (Y/N)?

Enter "Y" if you want to have the dwell times printed on the printer. Otherwise, enter "N" or just press the [ENTER] key. All dwell times in the queue will then be displayed on the CRT in the format shown below. If you selected hard copy, the same information will be printed on the printer. All values displayed are in seconds.

Channel Number	Dwell Time
N	XXX
M	YYY

Press Return to Continue

10. Readjust the Spectrophotometer calibration

    Once the high standard peak height is observed on the chart recorder from the dwell determination, adjust the calibration control to allow the high standard peak height to measure 90 to 95 % across the 5 volt scale. After the calibration has been adjusted, readjust the spectrophotometer to a baseline of 0.25 volts as in step 8.

11. Modify the Analytical Configuration File (ACF)

    a. To modify the ACF select "4" in response to the Menu "B" display. The program will prompt for a file name as follows:

    Enter Filename >
    Enter " Chloride" if you are using channel A or "ChloridB" if you are using channel B.

    Do you wish to add/delete channels (Y/N)? >
    Press [ENTER] to decline, then press [ENTER] until the frame with the dwell time is displayed. At this frame, enter "M" for modify. A series of prompts will display which is declined by [ENTER]. Proceed through the prompts until the dwell time prompt at which "Y" is entered.

    Enter "E" to exit the sequence and respond to the following prompt:

    Save modified file(Y/N)? >
    Enter "Y"

    Enter New Filename>
    Press [ENTER] to maintain old filename

    Do you want to activate this file (Y/N)? >
    Enter "Y" to activate the file

12. Prepare calibration standards

    a. STD 1 (1.0mg/L) = 0.1/100 of 1000 mg/L

    b. STD 2 (5.0mg/L) = 0.5/100 of 1000mg/L

    c. STD 3 (10.0mg/L) = 1.0/100 of 1000mg/L

    d. STD 4 (25.0mg/L) = 2.5/100 of 1000mg/L

    e. STD 5 (50.0mg/L) = 5.0/100 of 1000mg/L

    f. STD 6 (75.0mg/L) = 7.5/100 of 1000mg/L

g. STD 7 (100.0/mg/L) = 10.0/100 of 1000mg/L

h. ICV (50.0/mg/L) = 5.0/100 of 1000mg/L separate source

13. Create sample identification file

a. Under Primary Commands, select **A: Create File**

b. Then select option **1: Sample Identification File**

c. **Enter filename:** Month, Day, Year and Number of run for day. (Ex. February 11, 1991, 1st run of day = 02119101)

d. **Enter comment:** Name of parameter to be run and any applicable comments

e. **Apply constant dilution factors?** yes

f. **Prompt for dilution factors?** no [ENTER]

g. **Apply constant sample weights?** [ENTER]

h. **Prompt for sample weights?** [ENTER]

i. **Enter constant dilution factor:** 1

j. **Do you wish sequential sample ID number?** [ENTER}

k. **Enter sample ID for cup #2:** STD7

l. Enter the rest of the run at the prompt. Enter the entire initial calibration first with each standard in duplicate, separating each set with a blank cup. Start on cups # 3, 4 and 5 as blanks, then cup #6 as #STD1 then proceed in duplicate through #STD7 in ascending order.
Put the 50.0 mg/L ICV with #STD5. **Note:** A # sign must be put in front of each standard designator to identify it as a calibrant. Do not put the # sign in front of the ICV. After the calibration, put 3 blank cups before the first sample cups. Run the samples with a duplicate and matrix spike with every 10 sample analysis and conclude each 10 sample analysis with a 50 mg/L continuing calibration verification standard (CCV) and a continuing calibration blank (CCB). Separate each set of 10 with addition blanks and any known high samples with blanks to prevent carryover. Conclude the entire run with a CCV and CCB.

14. Prepare the sample tray according to the Sample Identification File

a. Remember cups # 1 and 2 will have STD7 in them followed

by 3 blank cups.

b. Fill each 2 mL sample cup completely.

c. Filter all turbid samples with a 0.45 micron in-line polyethylene filter connected to a 10 cc syringe.

d. Place the completed tray on the sampler with cup #1 in position to be sampled when the run begins. Press the "reset" button on the sampler to ensure the tray is in the correct position.

15. Inspect the reagents and the chart paper on the chart recorder to ensure there are sufficient quantities of both to supply the entire run.

16. Start the sample run

a. Return to the Primary Command menu and enter "C".

b. Select "1: Run" from the C menu and respond to the following prompts:

Enter Sample Designator (A/B) >
Enter channel selected in section 9d

Enter Sample ID Filename >
Enter the 8-digit sample identification file name created in section 13c.

Do You Wish to Collect Raw Data (Y/N)? >
Enter "Y" to the prompt. A raw data file will be created and preserved for the run.

Enter Analyst Initials >
Enter the analyst ID or name

Ready to Run (Y/N)? >
When "Y" is entered at the prompt, the sampling begins, so be sure the system is completely ready to start. the peak heights will be monitored and displayed on the computer screen automatically unless [ENTER] us pressed at the **Press Return to Stop Monitoring >** prompt.

17. If run must be aborted, press the F1 key to call up the System Abort menu. Select 1: Abort Sampler to stop the run. To re-start the run the aborted Plateau Data File and Raw Data File must be deleted at the prompts when re-activating the "1: Run" from the C menu.

18. Rerunning Samples

If peak heights are over range or distorted due to matrix or a sampling problem, reruns may be added to the end of the run as long as the sampler has not reached the last cup on the run by responding to the following prompts:

a. Enter "3" in response to the Menu C display.

Enter Sample Designator >
Enter channel selected in section 16b.

Enter Cup Number >
Enter the number of the cup to be redetermined. The program will repeat this prompt until pressing [ENTER] or until 40 cup numbers have been entered. The same cup number may be entered more than once to redetermine the same sample at different dilutions.

Cup Y Redetermination of X Enter Dilution Factor for "NNNNN" >
The program repeats this prompt for each cup that is added to the run. In this line, "X" represents the original cup number and "Y" is the new cup number being added to the run. NNNNN is the sample identifier for "X" being assigned to "Y" prefixed with an ampersand (&) to indicate on the report that it is a redetermination. Enter any number up to

10 characters in length to indicate any dilutions or simply press [ENTER] if no dilution is being made. When all prompts for dilutions have been responded, the program will automatically update the Sample Identification file and the sampler stop count and return to menu display.

Note: This entire entry sequence must be completed and the program returned to menu C before the system will recognize the request to run additional samples.

b. Prepare the additional sample cups using the dilutions indicated above and placing them in the correct positions on the sampler tray. **Warning:** The sampler arm and probe are still functioning and will not stop if your hand is there, so time the placement of cups carefully.

c. If time does not allow the automatic rerunning of samples, they may be rerun manually after the run is over by the following:

(1) At the Primary Commands select E: Utility Programs

(2) Select 3: Scale and press [ENTER] twice and monitor baseline on the chart recorder.

(3) Adjust the baseline to the voltage that it was between peaks

at the time sample for rerun was run in the original run

(4) Set the Sampler wash and sample settings (on the front of the unit) to the wash and sample times indicated in the Analytical Configuration File (see section 11)

(5) Pour appropriate dilutions of all samples to be rerun into sample cups and place on the next available tray positions. Conclude each ten reanalyzes with a CCV and CCB and record the samples and their dilutions on the original run printout.

(6) Check that there are sufficient reagent and chart paper quantities available for the re-analysis and press the start button on the front of the sampler.

(7) Record the voltages of the rerun peaks as they come across the spec and appear on the chart recorder.

(8) Follow Alpkem procedure for modifying a Plateau Data file and insert rerun voltages at the appropriate places in the original run to quantitate from original calibration.

Note: Be sure all records, recorded voltages and chart recordings are documented and included with original run. Clearly label the rerun peaks on the chart recorder with the sample ID # and the dilution. Be sure the rerun baseline is accurately set to the baseline of the original run or the differences must be added or subtracted from the inserted voltages. Be certain that all CCV and CCB data are within acceptable limits.

19. Obtaining Results

a. Select Menu **D: Print Hard Copy Commands** from the Primary Commands menu, then select **1: Plateau Data File** and respond to the following prompts:

Enter Filename >
Enter the 8-digit number used to create the Sample ID file for the run. Then Select **1: Final Results** from the menu displayed.

Suppress Flags on Report (Y/N)? >
Enter "Y" unless the flags explained in Appendix C of the Alpkem manual are useful in evaluating the data.

Redirect Printer Output (Y/N)? >
Enter "N" to this prompt unless it is helpful to preview the report on the computer screen before the report is printed. the printer will begin printing results immediately after "N" or will display the Plateau Data Reports menu again.

20. Before turning system off, run DI water through the system and all reagent lines for 15 minutes. After turning the systems off, remove all platens and release pump tube pressure from the pump rollers.

Operational Notes:

a. If excess noise is observed in the chloride determination, filter the chloride color reagent through a 0.45 um membrane filter.

b. Collect chloride waste in a separate container for subsequent disposal in an environmentally safe manner.

c. The mercury in the waste can be precipitated as mercuric sulfide to reduce the volume for disposal (see Alpkem procedure).

XII. CALCULATIONS

All results reported on the Plateau Data file are in concentration of mg/L. Alpkem dilutions may be put into the Sample Identification File and calculated by the computer, or manually calculated from the data at 1X. Solid leachates are express in mg/kg using the following formula:

$$\text{mg/kg} = \text{Alpkem result (mg/L)} \times \frac{\text{Final volume of leachate (mL)}}{\text{sample wt. (g)}}$$

XIII. QUALITY CONTROL REQUIREMENTS

A. The initial calibration will consist of the following requirements:

1.	Calibration Blank	< 1 mg/L
2.	7 calibration standards	correlation coefficient $\geq$ 0.995
3.	Separate source mid range ICV standard	$\pm$ 10 % of Theoretical Value

B. The sample run will consist of the following requirements:

1.	A Duplicate analysis every 10 samples	RPD $\leq$ 20% (if result is > 10 X detection limit)
2.	A Matrix Spike every 10 samples	MSR $\pm$ 25%
3.	A mid-range CCV after every 10 samples	$\pm$ 10% of Theoretical Value
4.	A CCB after every 10 samples	< 1 mg/L
5.	A CCV and CCB at the conclusion of the run with the same limits as above	

C. All reagents and standards made must be recorded in log books so as to be traceable to :

1. Manufacturer
2. Manufacturer lot #
3. Date received or made
4. Analyst making reagent
5. Log book and page reagent made, actual quantities used and accurate concentrations produced.

XIV. REFERENCES

A. Alpkem Method Number A303-S090-14

B. Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992. APHA-AWWA-WEF, p. 4-52

C. Methods for Chemical Analysis of Water and Wastes, March 1984, EPA-600/4-79-020, "Chloride", Method 325.2 (Automated Ferricyanide) Storet NO. 00940,

D. Zall, D.M., D.Fisher, and M.Q. Garner, "Photometric Determination of Chloride in Waster".

E. Methods for Chemical Analysis of Water and Wastes, March 1984, EPA-600/4-79-020, "Sample Preservation", p.xvii.

F. Technicon Industrial Method Number 99-70W, Chloride in Water and Wastewater, Technicon Instruments Corporation, Tarrytown, NY, Analytical Chemistry, Vol. 28 NO 11, p. 1665-1668.

PASI-Houston Lab
TOTAL ORGANIC CARBON, COMBUSTION/ HO-0-034
IR - SHIMADZU 5000 DATE: 01/23/96
HO-0-034
Authorization:

1.0 **SCOPE**: The method determines total organic carbon in water samples having carbonaceous matter which is either soluble or has particle size of 0.2mm or less. If the sample has been 0.45 filtered, the carbon can be reported as Dissolved Organic Carbon. The Shimadzu TOC is programmed to calibrated for two measurement ranges. The low range TOC scale is for determining TOC between 1 and 10 mg/l. The high range TOC scale is for determining TOC between 5 and 50 mg/l. Samples having higher TOC levels will be appropriately diluted.

2.0 **SUMMARY OF METHOD**: An acidified sample is purged for minimum of 3.5 minutes using zero grade compressed air or oxygen to remove inorganic forms of carbon. The purged sample is then automatically drawn into the instrument for combustion of carbon forms to carbon dioxide. The carbon dioxide produced is carried to an infrared detector. The detector signal is integrated and the concentration of the total organic carbon is determined.

3.0 **SAFETY ISSUES**: Each employee must adhere to safety requirements specified in each method Standard Operating Procedure (SOP). The laboratory maintains copies of Material Safety Data Sheets (MSDS) for each chemical on inventory. Any employee needing additional safety guidance should consult the lab Chemical Hygiene Plan, supervisor and/or the lab safety officer.

4.0 **SAMPLE HANDLING/PRESERVATION**: store in plastic or glass (glass preferred), acidify to pH <2 and refrigerate to 4 deg C, 28 day holding time.

5.0 **APPARATUS**:
- 5.1 Shimadzu TOC-5000 Total Organic Carbon Analyzer
- 5.2 Zero Grade Compressed Air or Oxygen
- 5.3 1000ul Fixed Volume Pipets.
- 5.4 Glass culture tubes having 5 to 20 ml capacity, used for purging CO2 from samples

6.0 **REAGENTS**:
- 6.1 **TOC Calibration Stock Standard, 2000 mg/L**: dissolve 2.1254g of dry potassium hydrogen phthalate (KHP - primary standard grade, dried at 105 deg C for 1.5 hours and cooled in a desiccator) into 100ml of Type II and dilute to a final volume of 500ml.
- 6.2 **Low Range CAL Stdn, 10.0 mg/l**: dilute 1.00ml of 2000 mg/L TOC Calibration Standard (from 6.1) to a final volume of 200ml (add 3 drops of conc. sulfuric acid before adjusting to 200ml.)
- 6.3 **High Range CAL Stdn, 50.0 mg/l**: dilute 5.00ml of 2000 mg/L TOC Calibration Standard (from 6.1) to a final volume of 200ml (add 3 drops of conc. sulfuric acid before adjusting to 200ml).
- 6.4 **Other standards for low and high range calibration** : the 25,0, 5.0 and 2.0mg/L: the standards can be prepared using the table below.

TOC, mg/L	2.0	5.0	10.0	25.0	50.0
ml of 6.1, 2000 mg/L	0.20	0.50	1.00	2.5	5.0
Final Vol, ml	200*	200*	200*	200*	200*

* Add 10 drops of 10 % sulfuric acid before adjusting to 200ml

6.5 Calibration Check Standards, the following standards are prepared separately from the Calibration Standards to verify calibration standard solutions (QC-5.0 AND QC-25.0):

7.0 INSTRUMENT OPERATION AND CALIBRATION PROCEDURE FOR THE TOC-5000:

7.1 All routine TOC-5000 operators must become familiar with the Instruction Manual, Total Organic Carbon Analyzer, Model TOC-5000, Shimadzu Dohrmann Corporation. The chapters of most importance are:

Chapter 3 - Measuring Principle - includes definitions and the calibration approaches available on the TOC-5000

Chapter 5 - Preparation - includes some of the daily operation principles

Chapter 3 - Measurement - includes description of more operations functions - i.e. setting calib. conditions

7.2 Instrument Warm Up: allow 20 minutes for warm-up and instrument baseline stabilization. Check condition of all tubing, plumbing, etc and perform daily maintenance steps so that optimum performance can be achieved. Air or Oxygen gas pressure entering the instrument should be 150 psi.

7.3 All samples and standards need to acidified and purged for 5.0 minutes prior to analysis by the TOC-5000. Standards are acidified as part of their preparation. Samples are typically acidified upon sample collection. Check all samples and standards and assure that the pH is 3 or less so that removal of CO2 during purging will be efficient. The purge gas flow needs to be vigorous to be efficient in removing CO2.

7.4 Calibration, Low Range: Using the 10.0, 5.0 and 2.0 mg/L CAL standards, calibrate the instrument according to the instru- ment calibration procedure outlined in the instrument manual.

7.5 Calibration, High Range: Using the 25.0 and 50.0 mg/L CAL standards, calibrate the instrument according to the instru- ment calibration procedure outlined in the instrument manual.

7.6 After calibration, the initial and continuing calibration verifications are performed using the QC-5.0 and QC-25 standards. They should agree within 10% of their true values (5.5-5.5 and 23.5-27.6 mg/l) for each range respectively.

7.7 Instrument Linearity Checks: Record and examine the each of the linearity correlation coefficients for the calibration standards and the blank. They should be 0.995 or greater. If they are not, perform system troubleshooting and corrective action.

7.8 Matrix spike (low range): Add 50ul of the 2000ppm Stock Stdn to 20.0ml of the sample (this is a 5.0ppm spike).

$$\text{percent recovery} = \frac{100 \times (\text{spike result,ppm} - \text{mean TOC,ppm})}{5.0 \text{ ppm}}$$

Matrix spikes (high range): Add 250ul of the 2000ppm Stock Stdn to 20.0ml of the sample (this is a 25.0 ppm spike).

NOTE: The mean TOC value used in all spike calculations needs to be the same value measured on the same dilution of the sample that is chosen to be spiked.

7.9 Matrix Spike/ Matrix Spike Dupl Rel. % Difference (RPD):

$$RPD = \frac{|\ \text{Mat Spk} - \text{Mat Spk Dup}\ |\ *\ 100}{\text{Average Matrix Spike}}$$

8.0 DATA RECORDING

8.1 Record all data for low range TOC analyses to the nearest 0.1 mg/L.
8.2 Report all mean TOC values to the nearest 0.1 value.
8.3 Report the percent recoveries for spikes, initial all data and include month, day and year on all data recording forms.

9.0 QUALITY CONTROL

9.1 Initially calibrate and verify calibration and linearity using the procedures in sections in 7.1-7.7.
9.2 Verify continuing calibration as in 7.6. after each set of ten samples and at the end of each run.
9.3 Run all samples in duplicate unless quadruplicates are re- quired. All analysis need to be purged minimally in duplicate.
9.4 Perform minimally one Matrix Spike and Matrix Spike Duplicate on each batch of 10 or less samples. Matrix spike results should range between 80 and 120%. If not, assume a matrix interference, analyze another sample in that same batch and if it does not fall between 80 and 120%, analyze a DI water spike and trouble shoot the spiking process and correct as necessary. Matrix spike duplicates should agree within 20 percent.

10.0 TOC DATA QUALITY ASSESSMENT CRITERIA

10.1 Calibration blank, run as sample: response = 0.1-0.6 mg/L
10.2 Calibration Verification Standards, QC-5.0 and QC-25.0 should agree within 10% of their true values (5.5-5.5 and 23.5-27.6 mg/l)
10.3 Matrix Spike recoveries should be 80-120%, Matrix Spike Duplicate results should agree within 80-120%.
10.4 1-10 samples per batch (analytical run).
10.5 CCB: Rerun Calib. Verification blank, response = (0.1-0.6)mg/L

11.0 REFERENCES:

11.1 Method 9060, Test Methods For Evaluating Solid Waste, Physical/ Chemical Methods (SW-846), Third Edition and applicable updates, Nov. 1986, USEPA Office of Solid Waste.
11.2 Method 415.1, Method for Chemical Analysis of Water And Wastes, Revised Edition, March 1983, USEPA Environmental Monitoring and Support Laboratory.
11.3 Method 5310 B, Standard Methods For The Examination Of Water And Wastewater, Seventeenth Edition, 1989, APHA-AWWA-WPCF.

11.4 Instruction Manual, Total Organic Carbon Analyzer, Model TOC-5000, Shimadzu Dohrmann Corporation (Initial Instrument installed 10/90 - Serial No. 286040203)

12.0 PERTINENT DEFINITIONS RELATING TO TOC:

Total Organic Carbon (TOC): carbon determined after nitrogen purge.

Total Carbon (TC): carbon determined on an unpurged portion of sample.

Dissolved Organic Carbon (DOC): the sample is 0.45micron filtered (often filtered in the field and labeled as such), organic carbon is determined is reported as dissolved.

Total Inorganic Carbon (TIC): found by subtracting the TOC from TC.

13.0 SOP POLICY ACKNOWLEDGEMENT - The following ETC Lab employees read this SOP, understand its components, acknowledge its existence.

Employee Name (Print)	Employee Signature	Acknowledgement Date
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* User name:   E_CLEMONS (25)              Queue:  PACEHOU_MAINSERVER-P66/DATAS*
* File name:                               Server: DATASVCS3                   *
* Directory:                                                                   *
* Description: Microsoft Word - HO-0-034.DOC                                   *
*              January 23, 1997                    6:20pm                      *
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*                                                                              *
*          EEEEE        CCC  L     EEEEE M   M  OOO  N   N  SSS              *
*          E           C   C L     E     MM MM O   O N   N S   S              *
*          E           C     L     E     M M M O   O NN  N S                  *
*          EEEE        C     L     EEEE  M M M O   O N N N  SSS               *
*          E           C     L     E     M   M O   O N  NN     S              *
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PASI-Houston Lab
TOTAL ORGANIC CARBON, COMBUSTION/ IR - SHIMADZU 5000
HO-0-034
Authorization:_____

HO-0-034
DATE: 01/23/96

1.0 **SCOPE**: The method determines total organic carbon in water samples having carbonaceous matter which is either soluble or has particle size of 0.2mm or less. If the sample has been 0.45 filtered, the carbon can be reported as Dissolved Organic Carbon. The Shimadzu TOC is programmed to calibrated for two measurement ranges. The low range TOC scale is for determining TOC between 1 and 10 mg/l. The high range TOC scale is for determining TOC between 5 and 50 mg/l. Samples having higher TOC levels will be appropriately diluted.

2.0 **SUMMARY OF METHOD**: An acidified sample is purged for minimum of 3.5 minutes using zero grade compressed air or oxygen to remove inorganic forms of carbon. The purged sample is then automatically drawn into the instrument for combustion of carbon forms to carbon dioxide. The carbon dioxide produced is carried to an infrared detector. The detector signal is integrated and the concentration of the total organic carbon is determined.

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Total Carbon (TC): carbon determined on an unpurged portion of sample.

Dissolved Organic Carbon (DOC): the sample is 0.45micron filtered (often filtered in the field and labeled as such), organic carbon is determined is reported as dissolved.

Total Inorganic Carbon (TIC): found by subtracting the TOC from TC.

13.0 SOP POLICY ACKNOWLEDGEMENT - The following ETC Lab employees read this SOP, understand its components, acknowledge its existence.

Employee Name (Print)	Employee Signature	Acknowledgement Date
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DATE: / /			ANALYST:		
LOW RANGE AREA	DI BLANK	2.0 mg/l	5.0mg/l	10.0 mg/l	Lin. Corr. coeff.
HIGH RANGE AREA	DI BLANK	25.0 mg/l	50.0mg/l		Lin. Corr. coeff.

SAMPLE ID	R1	R2	R3	R4	MEAN
QC- 5.0 (ICV)					
QC-25.0 (ICV)					
Dil Fac X					
Dil Fac X					
Dil Fac X					
Dil Fac X					
Dil Fac X					
Dil Fac X					
Dil Fac X					
Dil Fac X					
Dil Fac X					
Dil Fac X					

ID of SPIKES	Amt added	SPK R1	SPK R2	mean SPK	% Recov	REL % DIF
MS						
Dil Fac X						
MSD						
Fil Fac X						
DI H20 SPK						
DI H20 BLANK						

QC- 5.0 (CCV)						
QC-25.0 (CCV)						

METHOD NAME, UNIT __TOC, low range___ Instrument:[Shimadzu TOC-5000

TRUE VALUE : 5.0 mg/L SOURCE OF CONTROL : Dilution of QCTOC- 2000 to 5.0ppm

(25.0 mg/L) Dilution of QCTOC- 2000 to 25.0ppm

PREP DATE OF CONTROL: _____/_____/_____ EXPIRATION DATE: _____/_____/_____

CURRENT CONTROL STATISTICS _____

Mean _____ SD_____ UWL _____ LWL _____ UCL _____ LCL_____

	ANALYTE FOUND	PERCENT RECOVERY	DATE	ANALYST	EXCEEDS WL (Y or N)	EXCEEDS CL (Y or N)
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						

NEW CONTROL STATISTICS

Mean _____ SD_____ UWL _____ LWL _____ UCL _____ LCL_____

COMMENTS:

SD (stdn deviation) = calculated stdn deviation from 20 consecutive measurements
mean = calculated average from 20 consecutive measurements
UCL = upper control limit, +3 stdn dev. LCL = lower control limit, -3 stdn dev.
UWL = upper warning limit, +2 stdn dev. LWL = lower warning limit, -2 stdn dev.

1.0 METHOD NAME: Chemical Oxygen Demand (COD), Low Range (15 - 150mg/L) The method is applicable to aqueous samples having COD between 0 and 150 mg/L. If samples have COD above 150, use the COD high range method (COD 50 t0 600mg/L range). The detection limit is 15mg/L.

2.0 METHOD SUMMARY: Two ml of an aqueous sample is added to an ampule containing a fixed amount of chromic and sulfuric acid which contains a silver catalyst and mercuric sulfate to precipitate chlorides. The ampule is sealed, contents are mixed and digested on a block digester for two hours at 150 degrees C. The digested ampule is cooled. COD is measured on a Spectrophotometer at 620nm as a function of Chrome III.

3.0 SAMPLE HANDLING/PRESERVATION: Store in plastic or glass containers. Preserve samples with H2SO4 to pH less than 2. Keep refrigerated at 4 deg C. The recommended holding time is 28 days.

4.0 SAFETY ISSUES: Extreme caution must be used when adding the calibration standard and sample to the COD digestion solution vials. This is a very corrosive solution, and contains mercury and silver salts. The reaction is often exothermic, therefore, do not touch the vial with unprotected hands, as it may be hot. Exposure to the digestion solution will cause severe burns to the eyes, skin and respiratory tract. Refer to Material Safety Data Sheets (MSDS) for further information.

5.0 APPARATUS: Block COD Digester, Visible Spectrophotometer, 620nm.

6.0 REAGENTS:

6.1 Hach Low range COD vials.

6.2 Calibration Stock Standard, 10000mg/L COD : Prepare by dissolving 8.500g Potassium Hydrogen Phthalate in 500ml of DI water and dilute to 1000ml. Store under refrigeration. 1.0ml =10.00mg/L COD. Stable for approximately 12 months.

6.3 Quality Control Stock Standard, 10000mg/L COD: Prepared by the QC lab.

6.4 Quality Control Standard, 100mg/L COD : Prepare by the daily dilution of 1.00ml of 6.3 to a final volume of 100ml.

6.5 Daily Calibration Standards - 150, 100, 50mg/L COD: Dilute 3.00, 2.00 and 1.0ml respectively of the Calib Stock Standard (10000mg/L) to 200ml with DI water. Prepare fresh daily.

	Conc., mg/L COD	ml of 10000 mg/L stdn
final	50.0	1.00
volume,	100.0	2.00
200ml	150.0	3.00

7.0 PROCEDURE:

7.1 Standard Curve Preparation: The curve consists of six standards and a DI H2O blank (150, 125, 100, 75, 50, 25 and 0). For the 150, 100, 50 and DI Blank, add 2.0ml of each to marked COD vials,

cap tightly and mix. The 125, 75 and 25 are made as follows:
1) 125mg/L - add 1.00ml of 150 and 1.00ml of 100mg/L,
2) 75mg/L - add 1.00ml of 100 and 1.00ml of 50mg/L,
3) 25mg/L - add 1.00ml of 50 and 1.00ml of DI Blank.

7.2 Sample Preparation: Add 2.00ml of sample or 2.00ml of a diluted portion of the sample to a COD vial and cap tightly. Swirl the vial until the sample and the acid are well mixed. Record all dilution factors.

7.3 Recovery Spikes: To 10.0 ml sample or aliquot of sample diluted to 10.0, add 100ul (0.100ml) of Calib Stock Standard (10000mg/L) and mix in a disposable cup. Add 2.00 ml of this solution to the digestion vial. This is a 100 ppm spike.

7.4 Quality Control Standard, 100mg/L: Add 2.00ml of the QC Standard (solution 6.4) to a COD vial, cap tightly and and mix.

7.5 Block Digestion of Standards, Samples, Matrix Spikes, etc: Heat the all vials at 150 degC for two hours. Allow the vials to cool (do not open them), then proceed to measure COD using the Spec 21 at 620nm as per 7.6. If a COD vial becomes turbid upon cooling, re-warm it slghtly to remove turbity and measure while warm.

7.6 Absorbance Measurements of COD Calibration Standards, blanks and the QC standard at 620nm.

7.6.1 Adjust the Spec 21 absorbance to zero using the calibration blank.

7.6.2 Measure the absorbances of all of the calibration standards and the QC standard and record them.

7.6.3 Perform a linear regression on the calibration standard data as in 8.0. Calculate the correlation coefficient (it should be $\geq$ 0.995). Store the regression analysis and use it to calculate concentration of COD from Absorbance data as per 8.2

7.6.4 Measure absorbances of samples, matrix spikes, duplicates, etc. Calculate corresponding COD and record.

7.7 Matrix Spike Calculations:

$$\text{Percent Rec. (100ppm spk)} = \frac{100\ (\text{Spike Result, mg/L} - \text{mean sample result, mg/L})}{100.0\ \text{mg/L}}$$

Alternatively, a 50ppm spike is performed by adding 50ul(of10000) to 10.0ml of the sample. The percent recovery is calculated by:

$$\text{Percent Rec. (100ppm spk)} = \frac{100\ (\text{Spike Result, mg/L} - \text{mean sample result, mg/L})}{50.0\text{ppm}}$$

Record the actual level of spike added as 100 or 50 ppm.

8.0 REGRESSION using TI 60 calculator - example

Clear calculator - press **2nd** then **CSR**

data entry -	press X-Y	press E+	data #
(blank)	0 (ppm)	0.0 (ABS)	1
S1	25	0.010	2
S2	50	0.021	3
S3	75	0.031	4
S4	100	0.041	5
S5	125	0.051	6
S6	150	0.062	7

8.1 Calculation of Correlation Coefficient: press **2nd** and **Corr**
result - 0.9999 (record this)

8.2 Data Determination - convert sample ABS to mg/L COD:
Example: If ABS = 0.033,
key in 0.033 then press **2nd** and **X'**,
the calculator result should be **80.208** (ppb)
round the value off to **80** for recording purposes.

8.3 Additional Calculations: Round off all COD results to whole numbers, report data using no more that three significant figures, apply necessary dilution factors.

8.4 Should other calculators be used, refer to their operational instructions for linear regression analysis.

9.0 QUALITY CONTROL:

9.1 Perform the seven point once daily. Readjust the spec 21 zero and recalibrate as necessary using the same standards.

9.2 Analyze a COD control standard with every batch of 20 samples or less.

9.3 Analyze a lab duplicate every batch of 10 samples or less.

9.4 Record all data using the absorbance mode of the Spec 21, use the TI 60 calculator (or equivalent) and employ linear regression to calculate COD in the samples analyzed.

10.0 DATA QUALITY ACCEPTANCE:

10.1 The Correllation Coefficient must be $\geq$ 0.995. Duplicate results should be within a 20% agreement range unless values are < 50.

10.2 The QC standard Should be within its Control Limit or 100 $\pm$ 20 mg/L which ever is smaller.

10.3 Matrix spikes should range from 75-125% recovery unless a matrix interference is evident.

10.0 REFERENCE:

1) Method 410.4, COD Ampule Method, Methods for Chemical Analysis of Water and Wastes, March 1983, USEPA, 600/ 4-79-020.

2) Hach COD Ampule Method, Procedures for Water and Wastewater Analysis, 2nd Edition, 1987, Hach Company, Loveland.

COD,mg/L	0.0, Blank	25	50	75	100	125	150
absorbance							

Corr. Coeff.	Quant Limit = 15 mg/L	Date: (mm/dd/yy) ___/___/___	analyst

sample # / id	Dilution Factor	Chemical Oxygen Demand, mg/L initial absorb.	initial result	final result	Spike Amt added, 50 or 100?	Spike Amt Found, amt found	percent recovery
QC Check QCCOD-100							
01							
dup 01							
spike 01					50 100		
02							
03							
04							
05							
06							
07							
08							
09							
10							
11							
dup 11							
spike 11					50 100		
12							
13							
14							
15							
16							
17							
18							
19							
20							
QC Check QCCOD-100							
21							
dup 21							
spike 22					50 100		
23							

24							
25							

METHOD NAME, UNIT: COD, Low Range Instrument: manual digestion, spec 21

TRUE VALUE : 100 ppm SOURCE OF CONTROL : Daily Dilution of QCCOD-10000

PREP DATE OF CONTROL: ____/____/____ EXPIRATION DATE: ____/____/____

CURRENT CONTROL STATISTICS _____

Mean _____ SD_____ UWL _____ LWL _____ UCL _____ LCL_____

	ANALYTE FOUND	PERCENT RECOVERY	DATE	ANALYST	EXCEEDS CL (Y or N)	EXCEEDS WL (Y or N)
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						

NEW CONTROL STATISTICS

Mean _____ SD_____ UWL _____ LWL _____ UCL _____ LCL_____

COMMENTS:

SD = calculate standard deviations from 20 consecutive measurements
mean = calculated average from 20 consecutive measurements
UWL = upper warning limit, + 2 stdn dev. LWL = lower warning limit, - 2 stdn dev.
UCL = upper control limit, + 3 stdn dev. LCL = lower control limit, - 3 stdn dev.

1.0 METHOD SCOPE: High Range Chemical Oxygen Demand (COD), is applicable to aqueous samples having COD between 50 and 650 mg/L. If samples have COD below 50, use the COD low range method for better accuracy.

2.0 METHOD SUMMARY: Two ml of an aqueous sample is added to an ampule containing a fixed amount of chromic and sulfuric acid which contains a silver catalyst and mercuric sulfate to precipitate chlorides. The ampule is sealed, contents are mixed and digested on a block digester for two hours at 150 degreés C. The digested ampule is cooled. COD is measured on a Spectrophotometer at 620nm as a function of Chrome III.

3.0 SAMPLE HANDLING/PRESERVATION: Store in plastic or glass containers. Preserve samples with H2SO4 to pH less than 2. Keep refrigerated at 4 deg C. The recommended holding time is 28 days.

4.0 SAFETY ISSUES: Extreme caution must be used when adding the calibration standard and sample to the COD digestion solution vials. This is a very corrosive solution, and contains mercury and silver salts. The reaction is often exothermic, therefore, do not touch the vial with unprotected hands, as it may be hot. Exposure to the digestion solution will cause severe burns to the eyes, skin and respiratory tract. See Material Safety Data Sheets (MSDS) at back for further information.

5.0 APPARATUS: Block COD Digester, Visible Spectrophotometer, 620nm.

6.0 REAGENTS:

6.1 Hach High range COD vials (Hach Cat. #21258).

6.2 Calibration Stock Standard, 10000mg/L COD : Prepare by dissolving 8.500g Potassium Hydrogen Phthalate in 500ml of DI water and dilute to 1000ml. Store at 4 Deg C., 1.0ml =10.00mg/L COD. Stable for approximately 12 months.

6.3 Daily Calibration Standards: 600, 400, 200, 100 mg/L COD: Dilute 3.00, 2.00 and 1.00and 0.50ml respectively of the Calib Stock Standard (10000mg/L) to 50.0ml with DI water (see table below). Prepare fresh daily.

	Conc., mg/L COD	ml of 10000 mg/L stdn
final	100.0	0.50
volume,	200.0	1.00
50.0ml	400.0	2.00
	600.0	3.00

6.4 Quality Control Standard, 400mg/L COD: Prepare fresh daily by diluting 2.00 ml of the Quality Control Standard (10000mg/L) to 50.0ml with DI water. The Quality Control Standard (10000mg/L) is prepared by the QC Lab.

7.0 PROCEDURE:

7.1 Standard Curve Preparation: The curve consists of five standards and a DI H2O blank (600, 400, 200, 100, 50 and 0 mg/L). Add 2.00ml of each to appropriately marked COD vials, cap tightly and mix. The 50mg/L standard is made by adding 1.0ml of 100mg/L and 1.0ml of the DI water blank.

7.2 Quality Control Standard, 100mg/L: Add 2.00ml of the QC Stdn-400 (solution 6.4) to a COD vial, cap tightly and and mix.

7.3 Sample Preparation: Add 2.00ml of sample or 2.00ml of a diluted portion of the sample to a COD vial and cap tightly. Swirl the vial until the sample and the acid are well mixed. Record all dilution factors.

7.4 Recovery Spikes: To a 10.0 ml sample or aliquot of sample diluted to 10.0, add 250ul (0.250ml) of the Calib. Stock Standard (10000mg/L) and mix in a disposable cup. Add 2.00 ml of this solution to the COD vial and heat at 150 degC for two hours, cool and analyze as at 620nm on the Spec 21.

7.5 Block Digestion of Standards, Samples, Matrix Spikes, etc: Heat the all vials at 150 degC for two hours. Allow the vials to cool (do not open them), then proceed to measure COD using the Spec 21 at 620nm as per 7.6.

7.6 Absorbance Measurements of COD Calibration Standards, blanks and the QC standard at 620nm.

7.6.1 Adjust the Spec 21 absorbance to zero using the calibration blank.

7.6.2 Measure the absorbances of all of the calibration standards and the QC standard and record them.

7.6.3 Perform a linear regression on the calibration standard data as in 8.0. Calculate the correlation coefficient (it should be $\geq$ 0.995). Store the regression analysis and use it to calculate concentration of COD from Absorbance data as per 8.3.

7.6.4 Measure absorbances of samples, matrix spikes, duplicates, etc. and calculate corresponding COD and record.

7.7 Matrix Spike Calculations:

$$\text{Percent Rec. (250ppm spk)} = \frac{100\ (\text{Spike Result, mg/L} - \text{mean sample result, mg/L})}{250}$$

Alternatively, a 300ppm spike can be performed by adding 1.0ml of the 600mg/L standard and 1.0mg/L of the sample to the COD Vial. The percent recovery is calculated as:

$$\text{Percent Rec. (300ppm spk)} = \frac{100\ (\text{Spike Result, mg/L} - [\text{sample result, mg/L}/2])}{300}$$

Record the actual level of spike added as 250 or 300 ppm.

8.0 DATA RECORDING AND CALCULATIONS:

8.1 Linear Regression Analysis of the calibration will give the most accurate results. The concentrations of the blank and standards are plotted against their corresponding absorbances. Example calculations are carried out on a TI-60 Calculator.

Regression using TI 60 calculator - example

Clear calculator - press 2nd then CSR
data entry - press X-Y press E+ data #

blank	0 (ppm)	0.0	(ABS)	1
S1	50	0.024		2
S2	100	0.047		3
S3	200	0.095		4
S4	400	0.190		5
S5	600	0.282		6

8.2 Correlation coefficient - press 2nd and Corr
result - 0.9999 (record this)

8.2 COD concentration determination - for a sample ABS of 0.167: key in 0.033 then press 2nd and X', the calculator result should be 353.834 (ppm). Round the value off to 354 for recording purposes.

8.4 Other Calculations: Round off all COD results to whole numbers, report data using no more that three significant figures, apply necessary dilution factors.

9.0 QUALITY CONTROL:

9.1 Perform a six point calibration. Readjust the spec 21 zero and recalibrate the instrument as necessary using the same standards.

9.2 Analyze a COD control standard with every batch of 20 samples or less.

9.3 Analyze a lab duplicate every batch of 10 samples or less.

9.4 Record all data using the absorbance mode of the Spec 21, use the TI 60 or equivalent calculator and employ linear regression to calculate COD in the samples analyzed.

10.0 DATA QUALITY ACCEPTANCE:

10.1 The quality control standard must fall within its control limits.

10.2 The linearity correlation coefficient must be $\geq$ 0.995.

10.3 Duplicates must agree $\pm$ 20 percent, unless COD values are <80.

10.4 Spike recovery must be 75-125 percent unless a matrix interference is evident.

11.0 REFERENCES:

1) Method 410.4, COD Ampule Method, Methods for Chemical Analysis of Water and Wastes, March 1983, USEPA, 600/ 4-79-020.

2) Hach COD Ampule Method, Procedures for Water and Wastewater Analysis, 2nd Edition, 1987, Hach Company, Loveland.

COD,mg/L	0.0, Blank	50	100	200	400	600	
absorbance							

Corr. Coeff. _____ | Quant Limit = 40 mg/L | Date: (mm/dd/yy) ____/____/____ | analyst _____

sample # / id	Dilution Factor	Chemical Oxygen Demand, mg/L initial absorb.	initial result	final result	Spike Amt added, 250 or 300	Spike Amt Found, amt found	percent recovery
QC Check QCCOD-400							
01							
dup 01							
spike 01					250 300		
02							
03							
04							
05							
06							
07							
08							
09							
10							
11							
dup 11							
spike 11					250 300		
12							
13							
14							
15							
16							
17							
18							
19							
20							
QC Check CCOD-400							
21							
dup 21							
spike 21					250 300		

METHOD NAME, UNIT: **COD, High Range** Instrument: **manual digestion, spec 21**

TRUE VALUE : **400 mg/L** SOURCE OF CONTROL : Daily Dilution of QCCOD-10000

PREP DATE OF CONTROL: _____/_____/_____ EXPIRATION DATE: _____/_____/_____

CURRENT CONTROL STATISTICS _____

Mean _____ SD_____ UWL _____ LWL _____ UCL _____ LCL_____

	ANALYTE FOUND	PERCENT RECOVERY	DATE	ANALYST	EXCEEDS WL (Y or N)	EXCEEDS CL (Y or N)
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						

NEW CONTROL STATISTICS

Mean _____ SD_____ UWL _____ LWL _____ UCL _____ LCL_____

COMMENTS:

SD = calculate standard deviations from 20 consecutive measurements
mean = calculated average from 20 consecutive measurements
UWL = upper warning limit, + 2 stdn dev. LWL = lower warning limit, - 2 stdn dev.
UCL = upper control limit, + 3 stdn dev. LCL = lower control limit, - 3 stdn dev.